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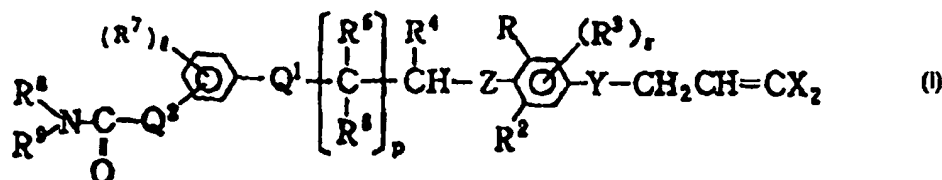
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<p>(21) International Application Number: PCT/JP97/00076 (22) International Filing Date: 17 January 1997 (17.01.97) (30) Priority Data: 8/10424 24 January 1996 (24.01.96) JP (71) Applicant (for all designated States except US): SUMITOMO CHEMICAL COMPANY, LIMITED [JP/JP]; 5-33, Kita- hama 4-chome, Chuo-ku, Osaka-shi, Osaka 541 (JP). (72) Inventors; and (75) Inventors/Applicants (for US only): Ikegami, Hiroshi [JP/JP]; 2-14-7, Mefu, Takarazuka-shi, Hyogo 665 (JP). HIROSE, Taro [JP/JP]; 1-13-35-1106, Higashinaka- jima, Higashiyodogawa-ku, Osaka-shi, Osaka 533 (JP). SUZUKI, Masaya [JP/JP]; 2-14-7, Mefu, Takarazuka-shi, Hyogo 665 (JP). IZUMI, Keiichi [JP/JP]; 2-10-1-154, Sonehigashi-machi, Toyonaka-shi, Osaka 561 (JP). SAKAMOTO, Noriyasu [JP/JP]; 2-10-2-232, Sonehigashi- machi, Toyonaka-shi, Osaka 561 (JP). TAKANO, Hirotaka [JP/JP]; 1-6-13, Fujigaoka, Sanda-shi, Hyogo 669-13 (JP). TAKADA, Yoji [JP/JP]; 2-10-4-454, Sonehigashi-machi, Toyonaka-shi, Osaka 561 (JP).</p>		<p>(74) Agents: AOYAMA, Tamotsu et al.; Aoyama & Partners, IMP Building, 3-7, Shiromi 1-chome, Chuo-ku, Osaka-shi, Osaka 540 (JP). (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published Without international search report and to be republished upon receipt of that report.</p>

(54) Title: DIHALOPROPENE COMPOUNDS, THEIR USE AS INSECTICIDES/ACARICIDES AND INTERMEDIATES FOR THEIR PRODUCTION



(57) Abstract

Dihalopropene compounds of general formula (I), wherein R, R² and R³ are each independently halogen, C₁-C₃ haloalkyl or C₁-C₃ alkyl; R⁴ is hydrogen or C₁-C₃ alkyl; R⁵ and R⁶ are each independently hydrogen, C₁-C₃ alkyl or trifluoromethyl; R⁷ is halogen, C₁-C₃ alkyl or trifluoromethyl; R⁸ and R⁹ have the meanings given in the description; Q¹ is a single bond or a linkage group defined in the description; Q² is a single bond, oxygen or NR¹⁴ in which R¹⁴ is hydrogen or C₁-C₃ alkyl; X's are each independently chlorine or bromine; Y is oxygen, NH or sulfur; Z is oxygen, sulfur or NR¹⁵ in which R¹⁵ is hydrogen or C₁-C₃ alkyl; l is an integer of 0 to 4; p is an integer of 0 to 6; and r is an integer of 0 to 2, have excellent insecticidal/acaricidal activity and are, therefore, useful as active ingredients of insecticidal-acaricidal agents.

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DESCRIPTION

DIHALOPROPENE COMPOUNDS, THEIR USE AS INSECTICIDES/ACARICIDES AND INTERMEDIATES FOR THEIR PRODUCTION

Technical Field

5 The present invention relates to dihalopropene compounds, their use and intermediates for their production.

Background Art

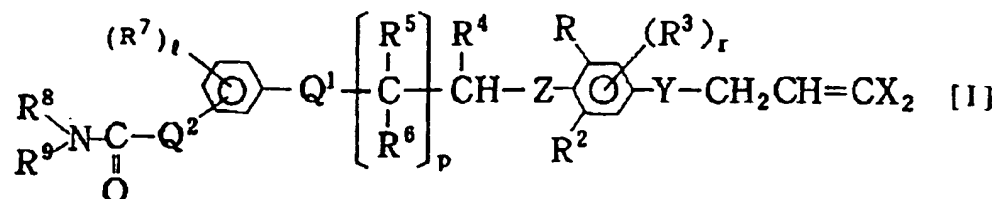
As disclosed in JP-A 49-1526/1974, for example, it is well known that some kinds of propene compounds can be used as active ingredients of insecticides.

10 In view of their insecticidal activity, however, it cannot always be said that these compounds are satisfactorily effective for the control of noxious insects.

Disclosure of Invention

The present inventors have intensively studied to find a compound having excellent insecticidal activity. As a result, they have found that particular dihalopropene
15 compounds have satisfactory insecticidal/acaricidal activity for the control of noxious insects, mites and ticks, thereby completing the present invention.

That is, the present invention provides dihalopropene compounds of the general formula:



20 (hereinafter referred to as the present compound(s)) and insecticidal/acaricidal agents containing them active ingredients,

wherein R, R² and R³ are each independently halogen, C₁-C₃ haloalkyl or C₁-C₃ alkyl;

R⁴ is hydrogen or C₁-C₃ alkyl;

R⁵ and R⁶ are each independently hydrogen, C₁-C₃ alkyl or trifluoromethyl;

R^7 is halogen, C_1 - C_3 alkyl or trifluoromethyl;

R^8 and R^9 are each independently hydrogen, C_1 - C_6 alkyl, C_1 - C_3 haloalkyl, C_3 - C_6 alkenyl, C_3 - C_6 haloalkenyl, C_3 - C_4 alkynyl, C_3 - C_4 haloalkynyl, C_4 - C_8 cycloalkyl-alkyl, C_6 - C_8 cycloalkenylalkyl or C_3 - C_4 alkoxyalkyl;

- 5 or C_3 - C_6 cycloalkynyl optionally substituted with C_1 - C_2 alkyl,
 or R^8 and R^9 are combined together at their ends to form C_2 - C_6 alkylene optionally substituted with C_1 - C_2 alkyl, or C_4 - C_6 alkenylene optionally substituted with C_1 - C_2 alkyl;

Q^1 is a single bond or T;

- 10 T is a group of the general formula:



wherein R^{10} and R^{11} are each independently hydrogen, C_1 - C_3 alkyl or trifluoromethyl; A is oxygen, $S(O)_n$, NR^{12} , $C(=O)G$ or $GC(=O)$ in which n is an integer of 0 to 2, R^{12} is hydrogen or C_1 - C_3 alkyl, G is oxygen or NR^{13} , and R^{13} is hydrogen or C_1 - C_3 alkyl;

- 15 and s is an integer of 0 to 6;

Q^2 is a single bond, oxygen or NR^{14} in which R^{14} is hydrogen or C_1 - C_3 alkyl;

X's are each independently chlorine or bromine;

Y is oxygen, NH or sulfur;

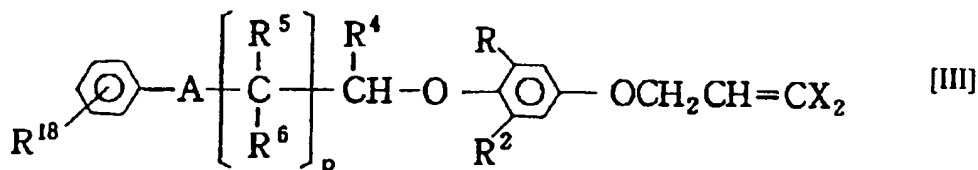
- 20 Z is oxygen, sulfur or NR^{15} in which R^{15} is hydrogen or C_1 - C_3 alkyl;

l is an integer of 0 to 4;

p is an integer of 0 to 6; and

r is an integer of 0 to 2.

The present invention further provides compounds of the general formula:



which are useful as intermediates for the production of some of the present compounds, wherein R and R² are each independently halogen, C₁-C₃ haloalkyl or C₁-C₃ alkyl;

R⁴ is hydrogen or C₁-C₃ alkyl;

5 R⁵ and R⁶ are each independently hydrogen, C₁-C₃ alkyl or trifluoromethyl;

R¹⁸ is carboxyl or amino;

A is oxygen, S(O)_n, NR¹², C(=O)G or GC(=O) in which n is an integer of 0 to 2, R¹² is hydrogen or C₁-C₃ alkyl, G is oxygen or NR¹³, R¹³ is hydrogen or C₁-C₃ alkyl;

10 X's are each independently chlorine or bromine; and
p is an integer of 0 to 6.

Among them are particularly provided compounds wherein R¹⁸ is carboxyl; compounds wherein A is oxygen; and compounds wherein R and R² are each independently halogen or C₁-C₃ alkyl, R⁴, R⁵ and R⁶ are all hydrogen, and p is 2 or 3.

15 Detailed Description of the Invention

The variables in the above formulas for the present compounds and/or the compounds of the general formula [III] can take the following specific examples.

Examples of the halogen atom represented by R, R², R³ or R⁷ may include fluorine, chlorine, bromine and iodine.

20 Examples of the C₁-C₆ alkyl group represented by R⁸ or R⁹ may include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, neopentyl, tert-pentyl, n-hexyl, isohexyl, 2-ethylbutyl, 1-methylpentyl, 1-ethylbutyl, 3-methylpentyl and 1,3-dimethylbutyl.

Examples of the C₂-C₆ alkylene group represented by R⁸ and R⁹, which are

combined together at their ends, may include ethylene, trimethylene, tetramethylene, penta-methylene and hexamethylene.

Examples of the C₄-C₆ alkenylene group represented by R⁸ and R⁹, which are combined together at their ends, may include 2-butenylene and 2-pentenylene.

5 Examples of the C₁-C₃ alkyl group represented by R, R², R³, R⁴, R⁵, R⁶, R⁷, R¹⁰, R¹¹, R¹², R¹³, R¹⁴ or R¹⁵ may include methyl, ethyl, n-propyl and isopropyl.

Examples of the C₁-C₂ alkyl group present in R⁸ or R⁹ may include methyl and ethyl.

10 Examples of the C₁-C₃ haloalkyl group represented by R, R², R³, R⁸ or R⁹ may include trifluoromethyl, difluoromethyl, bromodifluoromethyl, 2,2,2-trifluoroethyl, 2-fluoroethyl, 2-chloroethyl, 2-bromoethyl, 1-fluoroethyl, 1-chloroethyl, 1-bromoethyl, 2,2,3,3,3-pentafluoropropyl, 3,3,3-trifluoropropyl, 1-fluoropropyl, 2-chloropropyl and 3-bromopropyl.

15 Examples of the C₃-C₆ alkenyl group represented by R⁸ or R⁹ may include allyl, homoallyl, isopropenyl, 2-butenyl, 1-methyl-2-propenyl, prenyl, 3-methyl-3-butenyl, 1-ethyl-2-propenyl, 2-ethyl-2-propenyl, 2-pentenyl, 2-methyl-2-butenyl, 1-methyl-2-butenyl, 2-methyl-3-butenyl, 4-pentenyl, 1-methyl-3-butenyl, 1-ethyl-2-propenyl, 1-propyl-2-propenyl, 3-hexenyl, 2-isopropyl-2-propenyl, 2-ethyl-2-butenyl, 2-methyl-2-pentenyl, 1-ethyl-2-butenyl, 1-methyl-4-pentenyl, 1,3-dimethyl-2-butenyl,
20 2-hexenyl, 4-hexenyl, 5-hexenyl and 1-n-propyl-2-propenyl.

 Examples of the C₃-C₆ haloalkenyl group represented by R⁸ or R⁹ may include 3-chloro-2-propenyl, 3-bromo-2-propenyl, 2-chloro-2-propenyl, 2-bromo-2-propenyl, 3,3-dichloro-2-propenyl, 3,3-dibromo-2-propenyl, 3,3-difluoro-2-propenyl, 2-(chloromethyl)-2-propenyl, 4-chloro-2-butenyl, 4-chloro-2-butenyl, 3-chloro-4,4,4-
25 trifluoro-2-butenyl, 4-bromo-3-fluoro-4,4-difluoro-2-butenyl, 3,4,4,4-tetrafluoro-2-butenyl, 4,4-dichloro-3-butenyl, 4,4-dibromo-3-butenyl, 3-chloro-2-butenyl and 6,6-dichloro-5-hexenyl.

 Examples of the C₃-C₄ alkynyl group represented by R⁸ or R⁹ may include

2-propynyl, 1-methyl-2-propynyl, 2-butyne and 3-butyne.

Examples of the C₃-C₄ haloalkynyl group represented by R⁸ or R⁹ may include 3-chloro-2-propynyl, 3-bromo-2-propynyl, 4-chloro-2-butyne, 3-chloro-1-methyl-2-propynyl, 3-bromo-1-methyl-2-propynyl, 4-chloro-3-butyne and 4-bromo-3-butyne.

Examples of the C₃-C₄ alkoxyalkyl group represented by R⁸ or R⁹ may include ethoxymethyl, n-propyloxymethyl, isopropyloxymethyl, 2-methoxyethyl, 1-methoxyethyl, 2-ethoxyethyl, 1-ethoxyethyl, 3-methoxypropyl, 2-methoxypropyl, 1-methoxypropyl and 2-methoxy-1-methylethyl.

Examples of the C₃-C₆ cycloalkyl group optionally substituted with C₁-C₂ alkyl, which is represented by R⁸ or R⁹, may include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, 2-methylcyclohexyl, 3-methylcyclohexyl and 4-methylcyclohexyl.

Examples of the C₄-C₈ cycloalkylalkyl group represented by R⁸ or R⁹ may include cyclopropylmethyl, cyclobutylmethyl, 2-cyclopropylethyl, cyclopentylmethyl, cyclohexylmethyl and 2-cyclohexylethyl.

Examples of the C₆-C₈ cycloalkenylalkyl represented by R⁸ or R⁹ may include (1-cyclopentenyl)methyl, (1-cyclohexenyl)methyl and 2-(1-cyclohexenyl)ethyl.

The following are preferred examples of the present compounds:

compounds wherein R and R² are each independently halogen or C₁-C₃ alkyl, and r is 0;

compounds wherein R and R² are each independently chlorine, bromine or C₁-C₃ alkyl, and r is 0;

compounds wherein R and R² are both chlorine and r is 0;

compounds wherein Y and Z are both oxygen;

compounds wherein Q¹ is a single bond;

compounds wherein Q¹ is T and s is 0;

compounds wherein Q² is a single bond;

compounds wherein Q² is oxygen;

compounds wherein Q^2 is NR^{14} ;

compounds wherein Q^1 is T, s is 0, and Q^2 is a single bond;

compounds wherein A is oxygen;

compounds wherein A is oxygen, l is 0, p is an integer of 2 to 4, and R^4 , R^5
 5 and R^6 are all hydrogen;

compounds wherein R^8 and R^9 are each independently hydrogen, C_1 - C_6 alkyl, C_3 - C_6 alkenyl or C_3 - C_4 alkynyl, or R^8 and R^9 are combined together at their ends to form ethylene, trimethylene, tetramethylene, pentamethylene or butenylene.

The following are particularly preferred examples of the present compounds:

10 (3) 3,5-Dichloro-4-(4-(4-(1-piperidinylcarbonyl)phenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene;

(8) 3,5-Dichloro-4-(3-(4-(N,N-dipropylcarbamoyl)phenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene;

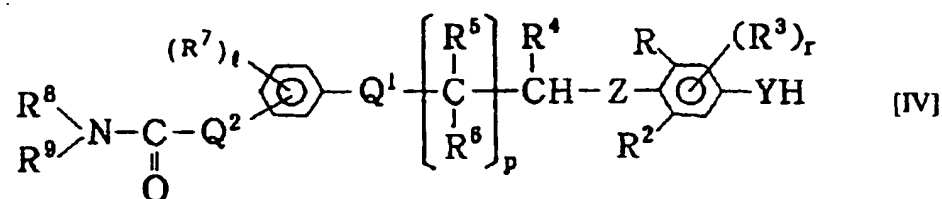
(11) 3,5-Dichloro-4-(3-(4-(N,N-di(2-propenyl)carbamoyl)phenoxy)propyl-
 15 oxy)-1-(3,3-dichloro-2-propenyloxy)benzene;

in which the above numbers in parentheses refer to the compound numbers of the present compounds described below.

The present compounds can be produced, for example, by the following production processes A to J.

20 (Production process A)

In this process, a compound of the general formula:



wherein R, R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , Q^1 , Q^2 , l, p, r, Y and Z are as defined above, is reacted with a halide compound of the general formula:



wherein X is as defined above and L is halogen (e.g., chlorine, bromine, iodine), mesyloxy or tosyloxy.

The reaction is preferably effected in an inert solvent in the presence of a
5 suitable base.

Examples of the solvent which can be used may include ketones such as acetone, methyl ethyl ketone and cyclohexanone; ethers such as 1,2-dimethoxyethane, tetrahydrofuran, dioxane and dialkyl (e.g., C₁-C₄) ether (e.g., diethyl ether, diisopropyl ether); N,N-dimethylformamide, dimethylsulfoxide, hexamethylphosphoric triamide,
10 sulfonane, acetonitrile, nitromethane; halogenated hydrocarbons such as dichloromethane, chloroform, 1,2-dichloroethane and chlorobenzene; hydrocarbons such as toluene, benzene and xylene; and water. If necessary, a mixture of these solvents can be used.

Examples of the base which can be used may include hydroxides of alkali
15 metals or alkaline earth metals, such as lithium hydroxide, sodium hydroxide, potassium hydroxide and calcium hydroxide; carbonates of alkali metals or alkaline earth metals, such as lithium carbonate, potassium carbonate, sodium carbonate and calcium carbonate; hydrides of alkali metals or alkaline earth metals, such as lithium hydride, sodium hydride, potassium hydride and calcium hydride; alkali metal alkoxides (e.g., C₁-C₄),
20 such as sodium methoxide, sodium ethoxide and potassium tert-butoxide; and organic bases such as triethylamine and pyridine. If necessary, catalysts such as ammonium salts (e.g., benzyltriethylammonium chloride) may be added to the reaction system at a ratio of 0.01 to 1 mole per mole of the compound of the general formula [IV].

The reaction temperature is usually set within the range of -20°C to +150°C
25 or the boiling point of a solvent used in the reaction, preferably -5°C to +100°C or the boiling point of a solvent used in the reaction.

The molar ratio of the starting materials and bases to be used in the reaction can be freely determined, but it is favorable to effect the reaction at an equimolar ratio or a ratio closer thereto.

After completion of the reaction, the reaction mixture is subjected to ordinary
5 post-treatments such as organic solvent extraction and concentration, and the desired compound of the present invention can be isolated. Furthermore, purification may be carried out, if necessary, by an ordinary technique such as chromatography, distillation or recrystallization.

(Production process B for the present compounds wherein Y is oxygen)

10 In this process, a compound of the general formula [IV] is reacted with an alcohol compound of the general formula:



wherein X is as defined above.

The reaction is preferably effected in the presence of a suitable dehydrating
15 agent in an inert solvent, if necessary.

Examples of the dehydrating agent which can be used may include dicyclohexylcarbodiimide, and dialkyl (e.g., C₁-C₄) azodicarboxylates (e.g., diethylazodicarboxylate, diisopropylazodicarboxylate)-trialkyl (e.g., C₁-C₂₀) phosphine or triarylphosphine (e.g., triphenylphosphine, trioctylphosphine, tributylphosphine).

20 Examples of the solvent which can be used may include hydrocarbons such as benzene, xylene and toluene; ethers such as diethyl ether, diisopropyl ether, tetrahydrofuran and dioxane; and halogenated hydrocarbons such as carbon tetrachloride, dichloromethane, chlorobenzene and dichlorobenzene.

The reaction temperature is usually set within the range of -20°C to +200°C
25 or the boiling point of a solvent used in the reaction.

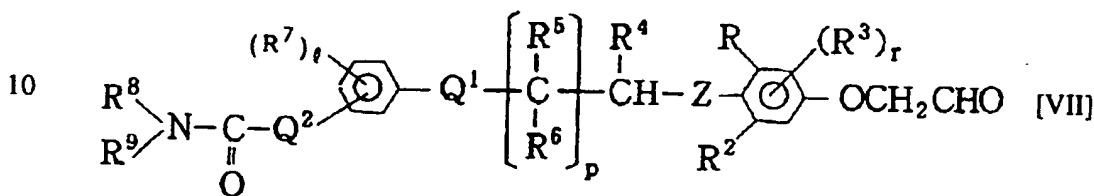
The molar ratio of the starting materials and dehydrating agents to be used in

the reaction can be freely determined, but it is favorable to effect the reaction at an equimolar ratio or a ratio closer thereto.

After completion of the reaction, the reaction mixture is subjected to ordinary post-treatments such as organic solvent extraction and concentration, and the desired compound of the present invention can be isolated. Furthermore, purification may be carried out, if necessary, by an ordinary technique such as chromatography, distillation or recrystallization.

(Production process C for the present compounds wherein Y is oxygen)

In this process, an aldehyde compound of the general formula:



wherein R, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, Q¹, Q², l, p, r, Y and Z are as defined above, is reacted with carbon tetrachloride or carbon tetrabromide.

The reaction is preferably effected in the presence of a suitable trialkylphosphine or triarylphosphine, and if necessary, in the presence of metal zinc, in an inert solvent.

Examples of the solvent which can be used may include hydrocarbons such as benzene, xylene and toluene; ethers such as diethyl ether, diisopropyl ether, tetrahydrofuran and dioxane; and halogenated hydrocarbons (exclusive of carbon tetrabromide and carbon tetrachloride) such as dichloromethane, 1,2-dichloroethane and chlorobenzene.

The reaction temperature is usually set within the range of -30°C to +150°C or the boiling point of a solvent used in the reaction.

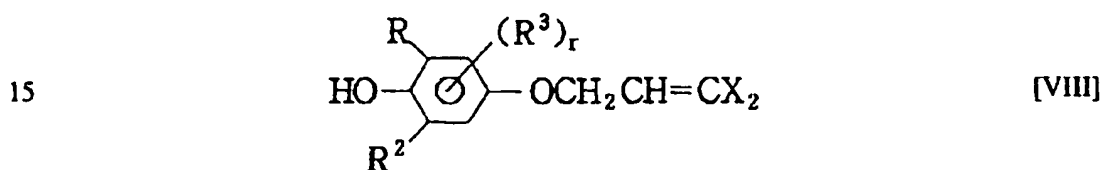
Examples of the trialkyl (e.g., C₁-C₂₀) phosphine or triarylphosphine, which can be used in the reaction, may include triphenylphosphine and trioctylphosphine. The metal zinc which is used, if necessary, is preferably in dust form.

The molar ratio of the starting materials and reagents to be used in the reaction can be freely determined, but the ratio is preferably such that carbon tetrabromide or tetrachloride, trialkylphosphine or triarylphosphine, and zinc are 2 moles, 2 or 4 moles (2 moles when zinc is used), and 2 moles, respectively, per mole of the aldehyde
 5 compound of the general formula [VII], or it is favorable to effect the reaction at a ratio closer thereto.

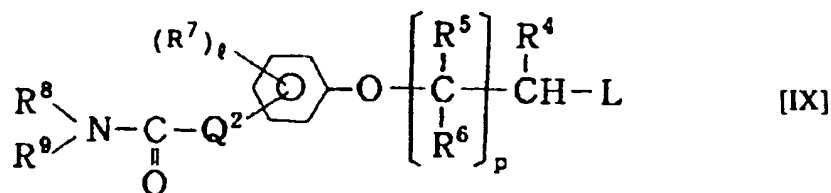
After completion of the reaction, the reaction mixture is subjected to ordinary post-treatments such as organic solvent extraction and concentration, and the desired compound of the present invention can be isolated. Furthermore, purification may be
 10 carried out, if necessary, by an ordinary technique such as chromatography, distillation or recrystallization.

(Production process D for the present compounds wherein Y and Z are both oxygen and Q¹ is T in which s is 0 and A is oxygen)

In this process, a compound of the general formula:



wherein R, R², R³, r and X are as defined above, is reacted with a compound of the general formula:



wherein R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, Q², l, p and L are as defined above.

20 The reaction is preferably effected in the presence of a suitable base in an inert solvent.

Examples of the solvent which can be used may include ketones such as acetone, methyl ethyl ketone and cyclohexanone; ethers such as 1,2-dimethoxyethane, tetrahydrofuran, dioxane and dialkyl (e.g., C₁-C₄) ethers (e.g., diethyl ether, diisopropyl ether); N,N-dimethylformamide, dimethylsulfoxide, hexamethylphosphoric triamide, sulforane, acetonitrile, nitromethane; halogenated hydrocarbons such as dichloromethane, chloroform, 1,2-dichloroethane and chlorobenzene; hydrocarbons such as toluene, benzene and xylene; and water. If necessary, a mixture of these solvents can be used.

Examples of the base which can be used may include hydroxides of alkali metals or alkaline earth metals, such as lithium hydroxide, sodium hydroxide, potassium hydroxide and calcium hydroxide; carbonates of alkali metals or alkaline earth metals, such as lithium carbonate, potassium carbonate, sodium carbonate and calcium carbonate; hydrides of alkali metals or alkaline earth metals, such as lithium hydride, sodium hydride, potassium hydride and calcium hydride; alkali metal alkoxides (e.g., C₁-C₄) such as sodium methoxide, sodium ethoxide and potassium tert-butoxide; organic bases such as triethylamine and pyridine. If necessary, catalysts such as ammonium salts (e.g., benzyltriethylammonium chloride) may be added to the reaction system at a ratio of 0.01 to 1 mole per mole of the compound of the general formula [VIII].

The reaction temperature is usually set within the range of -20°C to +150°C or the boiling point of a solvent used in the reaction, preferably -5°C to +100°C or the boiling point of a solvent used in the reaction.

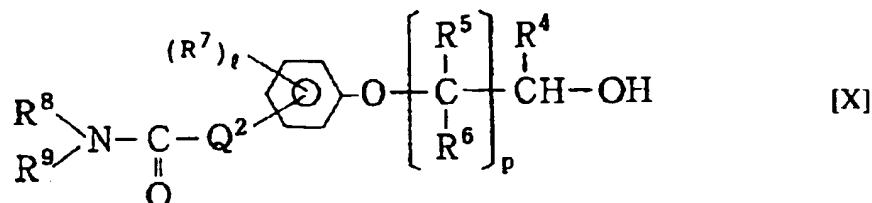
The molar ratio of the starting materials and bases to be used in the reaction can be freely determined, but it is favorable to effect the reaction at an equimolar ratio or a ratio closer thereto.

After completion of the reaction, the reaction mixture is subjected to ordinary post-treatments such as organic solvent extraction and concentration, and the desired compound of the present invention can be isolated. Furthermore, purification may be carried out, if necessary, by an ordinary technique such as chromatography, distillation or

recrystallization.

(Production process E for the present compounds wherein Y and Z are both oxygen and Q¹ is T in which s is 0 and A is oxygen)

In this process, a compound of the general formula [VIII] is reacted with an
5 alcohol compound of the general formula:



wherein R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, Q², l and p are as defined above.

The reaction is preferably effected in the presence of a suitable dehydrating agent in an inert solvent, if necessary.

10 Examples of the dehydrating agent which can be used may include dicyclohexylcarbodiimide, and dialkyl (e.g., C₁-C₄) azodicarboxylates (e.g., diethylazodicarboxylate, diisopropylazodicarboxylate)-trialkyl (e.g., C₁-C₂₀) phosphine or triarylphosphine (e.g., triphenylphosphine, trioctylphosphine, tributylphosphine).

Examples of the solvent which can be used may include hydrocarbons such
15 as benzene, xylene and toluene; ethers such as diethyl ether, diisopropyl ether, tetrahydrofuran and dioxane; and halogenated hydrocarbons such as carbon tetrachloride, dichloromethane, chlorobenzene and dichlorobenzene.

The reaction temperature is usually set within the range of -20°C to +200°C or the boiling point of a solvent used in the reaction.

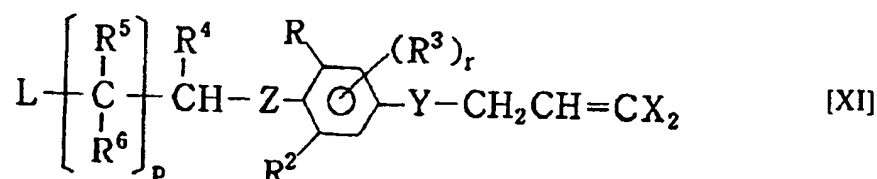
20 The molar ratio of the materials and dehydrating agents to be used in the reaction can be freely determined, but it is favorable to effect the reaction at an equimolar ratio or a ratio closer thereto.

After completion of the reaction, the reaction mixture is subjected to ordinary post-treatments such as organic solvent extraction and concentration, and the desired

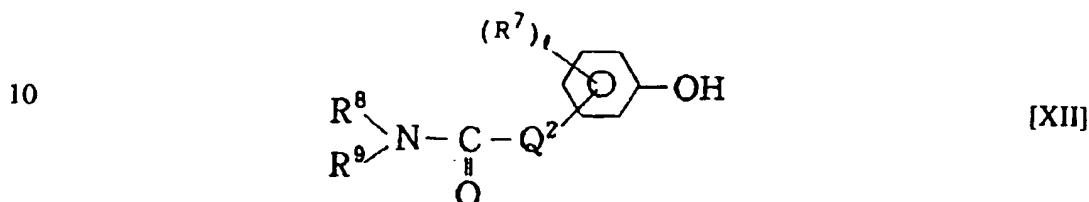
compound of the present invention can be isolated. Furthermore, purification may be carried out, if necessary, by an ordinary technique such as chromatography, distillation or recrystallization.

(Production process F for the present compounds wherein Q^1 is T in which s is 0 and A is oxygen)

In this process, a compound of the general formula:



wherein R , R^2 , R^3 , R^4 , R^5 , R^6 , p , r , X , Y , Z and L are as defined above, is reacted with a compound of the general formula:



wherein R^7 , R^8 , R^9 , Q^2 and l as defined above.

The reaction is preferably effected in the presence of a suitable base in an inert solvent.

Examples of the solvent which can be used may include ketones such as acetone, methyl ethyl ketone and cyclohexanone; ethers such as 1,2-dimethoxyethane, tetrahydrofuran, dioxane and dialkyl (e.g., C_1 - C_4) ethers (e.g., diethyl ether, diisopropyl ether); N,N -dimethylformamide, dimethylsulfoxide, hexamethylphosphoric triamide, sulforane, acetonitrile, nitromethane; halogenated hydrocarbons such as dichloromethane, chloroform, 1,2-dichloroethane and chlorobenzene; hydrocarbons such as toluene, benzene and xylene; and water. If necessary, a mixture of these solvents can be used.

Examples of the base which can be used may include hydroxides of alkali metals or alkaline earth metals, such as lithium hydroxide, sodium hydroxide, potassium hydroxide and calcium hydroxide; carbonates of alkali metals or alkaline earth metals, such as lithium carbonate, potassium carbonate, sodium carbonate and calcium carbonate; hydrides of alkali metals or alkaline earth metals, such as lithium hydride, sodium hydride, potassium hydride and calcium hydride; alkali metal alkoxides (e.g., C₁-C₄) such as sodium methoxide, sodium ethoxide and potassium tert-butoxide; organic bases such as triethylamine and pyridine. If necessary, catalysts such as ammonium salts (e.g., benzyltriethylammonium chloride) may be added to the reaction system at a ratio of 0.01 to 1 mole per mole of the compound of the general formula [XII].

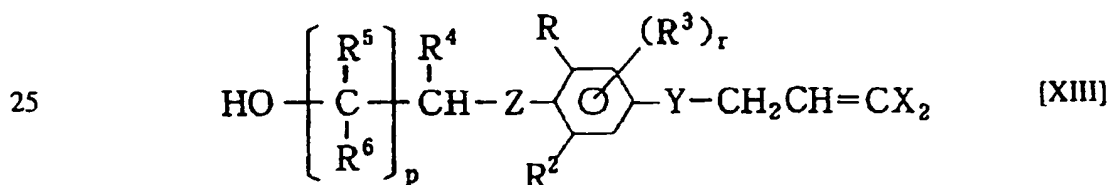
The reaction temperature is usually set within the range of -20°C to +150°C or the boiling point of a solvent used in the reaction, preferably -5°C to +100°C or the boiling point of a solvent used in the reaction.

The molar ratio of the starting materials and bases to be used in the reaction can be freely determined, but it is favorable to effect the reaction at an equimolar ratio or a ratio closer thereto.

After completion of the reaction, the reaction mixture is subjected to ordinary post-treatments such as organic solvent extraction and concentration, and the desired compound of the present invention can be isolated. Furthermore, purification may be carried out, if necessary, by an ordinary technique such as chromatography, distillation or recrystallization.

(Production process G for the present compounds wherein Q¹ is T in which s is 0 and A is oxygen)

In this process, a compound of general formula:



wherein R, R², R³, R⁴, R⁵, R⁶, p, r, X, Y and Z are as defined above, is reacted with a compound of the general formula [XII].

The reaction is preferably effected in the presence of a suitable dehydrating agent in an inert solvent, if necessary.

5 Examples of the dehydrating agent which can be used may include dicyclohexylcarbodiimide, and dialkyl (e.g., C₁-C₄) azodicarboxylates (e.g., diethylazodicarboxylate, diisopropylazodicarboxylate)-trialkyl (e.g., C₁-C₂₀) phosphine or triarylphosphine (e.g., triphenylphosphine, trioctylphosphine, tributylphosphine).

10 Examples of the solvent which can be used may include hydrocarbons such as benzene, xylene and toluene; ethers such as diethyl ether, diisopropyl ether, tetrahydrofuran and dioxane; and halogenated hydrocarbons such as carbon tetrachloride, dichloromethane, chlorobenzene and dichlorobenzene.

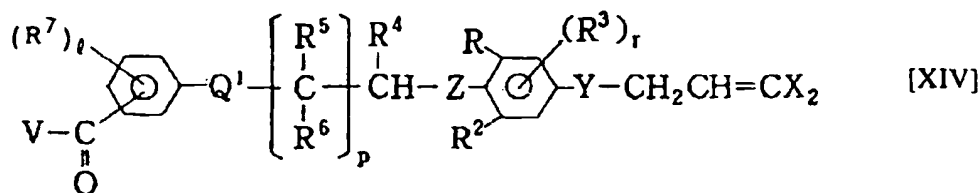
The reaction temperature is usually set within the range of -20°C to +200°C or the boiling point of a solvent used in the reaction.

15 The molar ratio of the materials and dehydrating agents to be used in the reaction can be freely determined, but it is favorable to effect the reaction at an equimolar ratio or a ratio closer thereto.

20 After completion of the reaction, the reaction mixture is subjected to ordinary post-treatments such as organic solvent extraction and concentration, and the desired compound of the present invention can be isolated. Furthermore, purification may be carried out, if necessary, by an ordinary technique such as chromatography, distillation or recrystallization.

(Production process H for the present compounds wherein Q² is a single bond)

25 In this process, a carboxylic acid compound of the general formula:



wherein R, R², R³, R⁴, R⁵, R⁶, R⁷, Q¹, l, p, r, X, Y and Z are as defined above and V is chlorine, bromine, hydroxyl, methoxy, ethoxy, propyloxy or 1-imidazolyl, is reacted with an amine compound of the general formula:



wherein R⁸ and R⁹ are as defined above.

(i) In the case where V in the general formula [XIV] is chlorine, bromine or 1-imidazolyl, examples of the reaction solvent which can be used may include ethers such as diethyl ether, tetrahydrofuran and dioxane; aromatic hydrocarbons such as benzene, toluene, xylene, chlorobenzene and pyridine; hydrocarbons such as n-hexane, n-heptane and cyclohexane; halogenated hydrocarbons such as methylene chloride, chloroform, carbon tetrachloride and 1,2-dichloroethane; esters such as ethyl acetate and methyl acetate; water; nitriles such as acetonitrile; polar solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone and dimethylsulfoxide; and mixtures thereof.

The reaction temperature is usually set within the range of -20°C to +150°C or the boiling point of a solvent used in the reaction, preferably 0°C to 50°C.

The reaction is usually effected in the presence of a base such as sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, triethylamine or pyridine at a ratio of 1 to 10 moles per mole of the compound of the general formula [XIV].

When two phase reaction is effected with water as a solvent, the use of a phase transfer catalyst such as tetra-n-butylammonium bromide or benzyltriethylammo-

nium chloride makes it possible to raise the reaction rate.

(ii) In the case where V in the general formula [XIV] is hydroxyl, methoxy, ethoxy or propoxy, the reaction is usually effected without any solvent, or in a polar solvent such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone
5 or dimethylsulfoxide, or in an aromatic hydrocarbon solvent such as benzene, toluene, xylene or chlorobenzene, at a reaction temperature of 50° to 250°C.

If necessary, as a reaction catalyst, an acidic substance such as sulfuric acid, benzenesulfonic acid, p-toluenesulfonic acid or active silica gel, or a basic substance such as pyridine, triethylamine, sodium methoxide, sodium ethoxide or active alumina can be
10 used at a weight which is 0.0001 to 1 time as much as the weight of the compound of general formula [XIV].

The molar ratio of the materials to be used in the reaction can be freely determined, but it is favorable to effect the reaction at an equimolar ratio or a ratio closer thereto.

15 (iii) In the case where V in the general formula [XIV] is hydroxyl, the following process can be used in the production.

That is, a carboxylic acid compound of the general formula [XIV] is usually reacted with an amine compound of the general formula [XV] in the presence or absence of an inert organic solvent, thereby causing condensation by dehydration to give the
20 desired compound of the present invention. Examples of the dehydrating agent may include carbodiimides such as dicyclohexylcarbodiimide and 1-ethyl-3-(3-dimethylamino-propyl)carbodiimide; and inorganic dehydrating agents such as silicon tetrachloride. Examples of the inert organic solvent may include hydrocarbons such as n-pentane, n-hexane, n-heptane and cyclohexane; aromatic hydrocarbons such as benzene, toluene,
25 xylene, chlorobenzene, pyridine and o-dichlorobenzene; halogenated hydrocarbons such as methylene chloride, chloroform, carbon tetrachloride and 1,2-dichloroethane; esters such as ethyl acetate and methyl acetate; amides such as N,N-dimethylformamide, N,N-dimethylacetamide and N-methylpyrrolidone; nitriles such as acetonitrile; and ethers such

as diethyl ether, tetrahydrofuran and dioxane.

The reaction temperature is usually set within the range of -20°C to $+150^{\circ}\text{C}$ or the boiling point of a solvent used in the reaction.

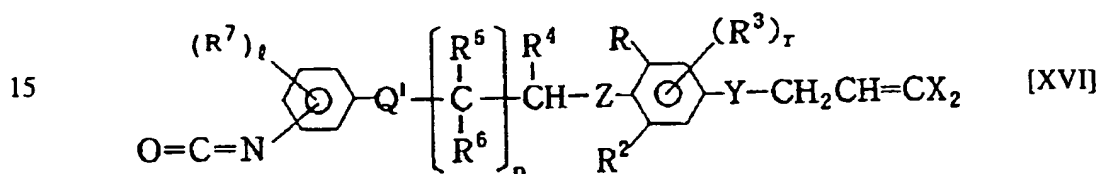
The molar ratio of the materials and dehydrating agents to be used in the
5 reaction can be freely determined, but it is favorable to effect the reaction at an equimolar ratio or a ratio closer thereto.

After completion of the reaction in case (i), (ii) or (iii), the reaction mixture is subjected to ordinary post-treatments such as organic solvent extraction and concentra-
tion, and the desired compound of the present invention can be isolated. Furthermore,
10 purification may be carried out, if necessary, by an ordinary technique such as chroma-
tography, distillation or recrystallization.

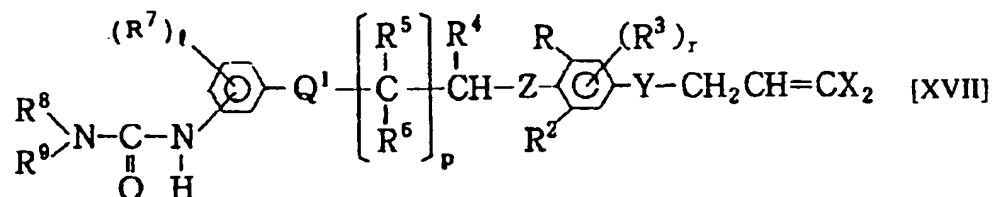
(Production process I for the present compounds wherein Q^2 is NR^{14})

(The first step of the production process I)

In this process, an isocyanate compound of the general formula:



wherein R , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , Q^1 , l , p , r , X , Y and Z are as defined above, is reacted with an amine compound of the general formula [XV] to give an urea derivative compound of the general formula:



wherein R , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , Q^1 , l , p , r , X , Y and Z are as defined above, which is included in the present compounds.

Examples of the solvent which can be used may include hydrocarbons such as benzene and toluene; ethers such as diethyl ether, tetrahydrofuran and dioxane; polar solvents such as N,N-dimethylformamide, dimethylsulfoxide and hexamethylphosphoric acid triamide; halogenated hydrocarbons such as methylene chloride, chloroform, 1,2-dichloroethane and chlorobenzene; acetonitrile; and nitromethane. If necessary, a mixture of these solvents can be used.

The reaction temperature is usually set within the range of -20°C to the boiling point of a solvent used in the reaction, preferably -5°C to the boiling point of a solvent used in the reaction.

The molar ratio of the materials to be used in the reaction can be freely determined, but it is favorable to effect the reaction at an equimolar ratio or a ratio closer thereto.

After completion of the reaction, the reaction mixture is subjected to ordinary post-treatments such as organic solvent extraction and concentration, and the desired compound of the present invention wherein R^{14} is H can be isolated. Furthermore, purification may be carried out, if necessary, by an ordinary technique such as chromatography, distillation or recrystallization.

(The second step of the production process I)

In this process, an urea derivative compound of the general formula [XVII] wherein R^{14} is H is reacted with a halogenated compound of the general formula:



wherein R^{14} is as defined above but it does not represent hydrogen, and L^1 is halogen (e.g., chlorine, bromine, iodine), to give the present compounds wherein R^{14} is not hydrogen.

The reaction is preferably effected in the presence of an appropriate catalyst in a solvent having no influence thereon.

Examples of the solvent which can be used may include ketones such as acetone and methyl ethyl ketone; hydrocarbons such as benzene and toluene; ethers such as diethyl ether, tetrahydrofuran and dioxane; halogenated hydrocarbons such as methylene chloride, chloroform, 1,2-dichloroethane and chlorobenzene; acetonitrile; nitromethane; and pyridine. If necessary, a mixture of these solvents can be used.

Examples of the base which can be used may include carbonates of alkali metals, such as potassium carbonate; hydrides of alkali metals, such as sodium hydride; and organic bases such as sodium methoxide, sodium ethoxide, triethylamine and pyridine.

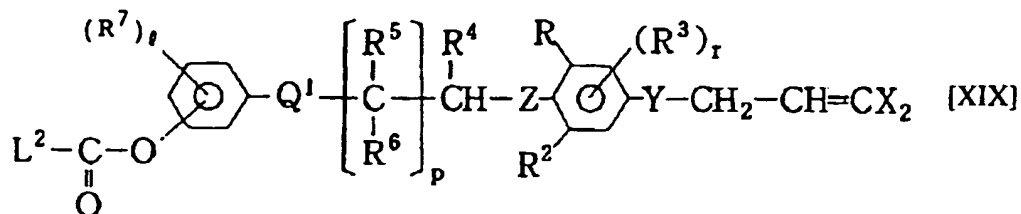
The reaction temperature is usually set within the range of -10°C to the boiling point of a solvent used in the reaction.

The molar ratio of the materials to be used in the reaction can be freely determined, but it is preferred that the compound of the general formula [XVIII] and the base are used at ratios of 1 to 2 moles and 0.9 to 20 moles, respectively, per mole of the urea derivative compound of the general formula [XVII].

After completion of the reaction, the reaction mixture is subjected to ordinary post-treatments such as organic solvent extraction and concentration, and the desired compound of the present invention can be isolated. Furthermore, purification may be carried out, if necessary, by an ordinary technique such as chromatography, distillation or recrystallization.

(Production process J for the present compounds wherein Q^2 is oxygen)

In this process, a compound of the general formula [XIX] is reacted with a compound of the general formula:



wherein R, R², R³, R⁴, R⁵, R⁶, R⁷, Q¹, l, p, r, X, Y and Z are as defined above, and L² is chlorine or bromine, is reacted with an amine compound of the general formula [XV].

The reaction is preferably effected in the presence of an appropriate catalyst in a solvent having no influence thereon.

5 Examples of the base which can be used may include carbonates of alkali metals, such as potassium carbonate; and organic bases such as triethylamine and pyridine. If necessary, a catalyst such as ammonium salts (e.g., benzyltriethylammonium chloride) may be added to the reaction system.

 Examples of the solvent which can be used may include ketones such as
10 acetone and methyl ethyl ketone; hydrocarbons such as benzene and toluene; ethers such as diethyl ether, tetrahydrofuran and dioxane; halogenated hydrocarbons such as methylene chloride, chloroform, 1,2-dichloroethane and chlorobenzene; acetonitrile; and nitromethane. If necessary, a mixture of these solvents or a mixture of these solvents and water can be used.

15 The reaction temperature is usually set within the range of -20°C to the boiling point of a solvent used in the reaction, preferably -5°C to the boiling point of a solvent used in the reaction.

 The molar ratio of the materials to be used in the reaction can be freely determined, but it is favorable to effect the reaction at an equimolar ratio or a ratio closer
20 thereto.

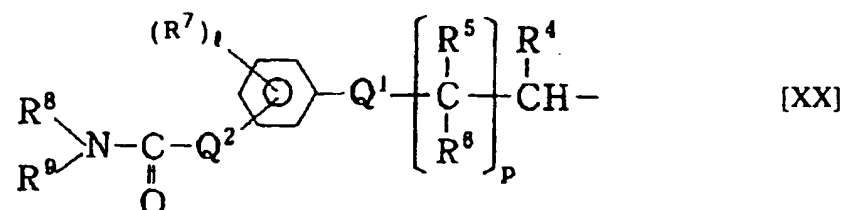
 After completion of the reaction, the reaction mixture is subjected to ordinary post-treatments such as organic solvent extraction and concentration, and the desired compound of the present invention can be isolated. Furthermore, purification may be carried out, if necessary, by an ordinary technique such as chromatography, distillation or
25 recrystallization.

 When any one of the present compounds has an asymmetric carbon atom, it is to be construed to include its optically active isomers (i.e., (+)-form and (-)-form) having biological activity and their mixtures at any ratio. When any one of the present

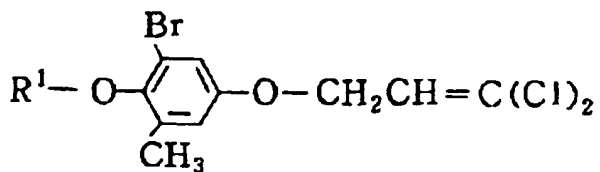
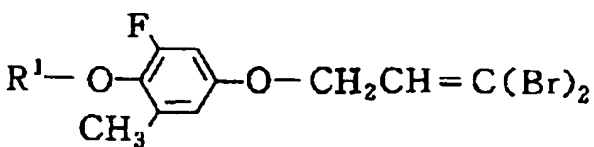
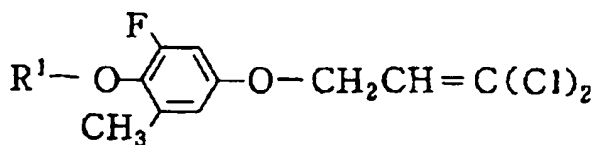
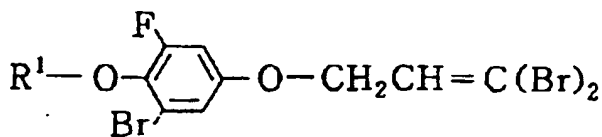
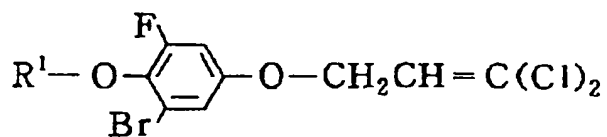
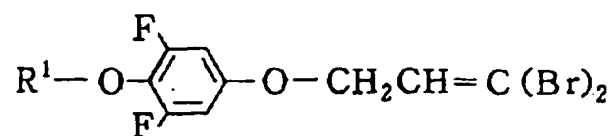
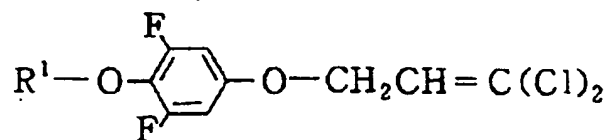
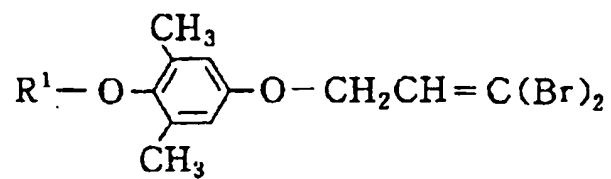
compounds exhibits geometrical isomerism, it is to be construed to include its geometrical isomers (i.e., cis-form and trans-form) and their mixtures at any ratio.

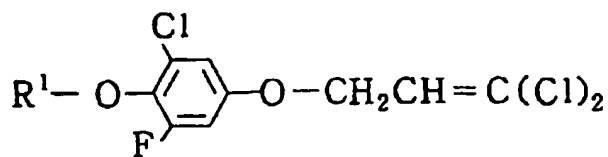
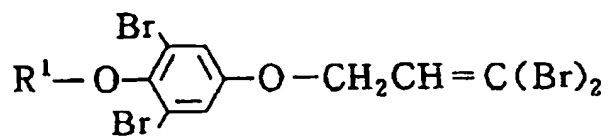
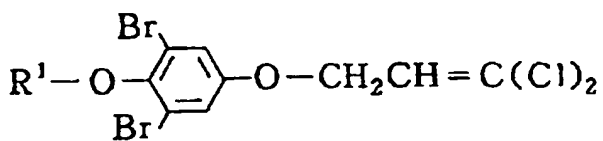
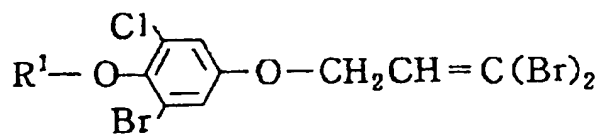
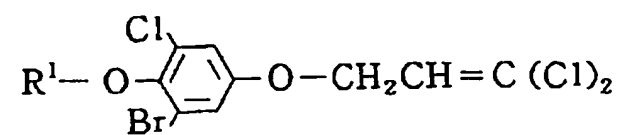
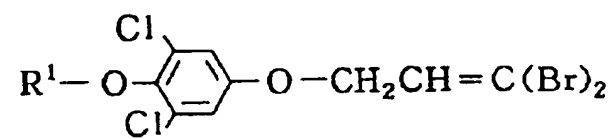
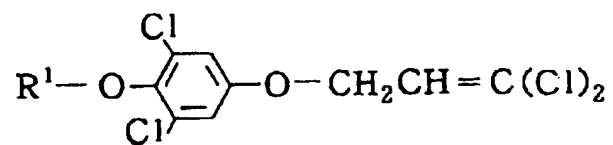
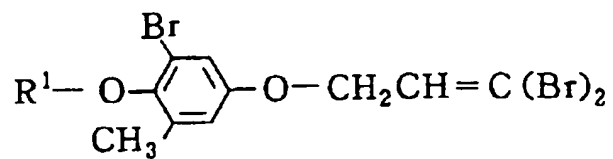
The following are specific examples of the present compounds; however, the present invention is not limited to these examples.

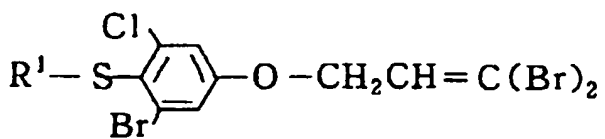
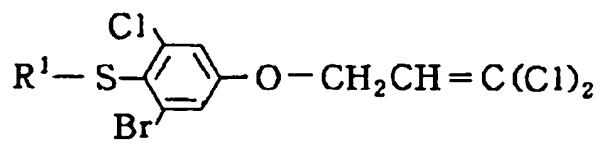
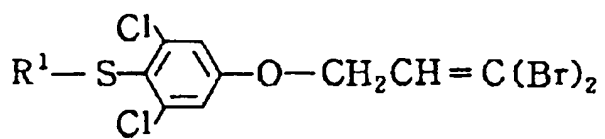
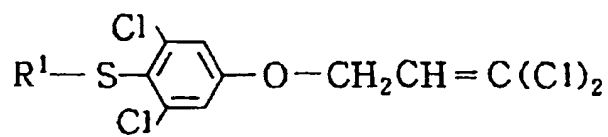
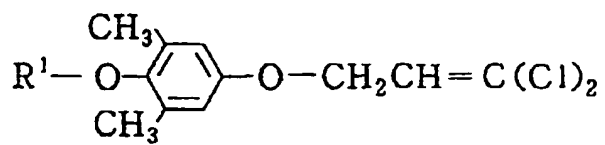
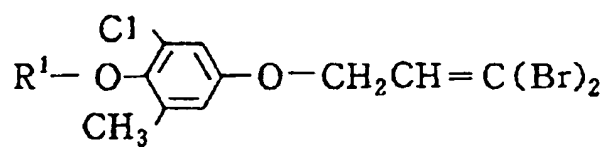
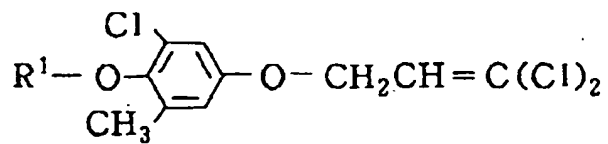
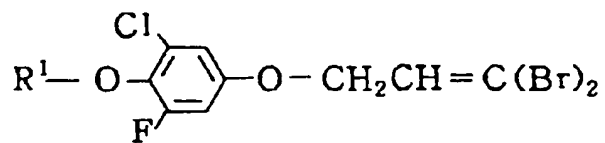
5 In these examples, R^1 is of the formula:

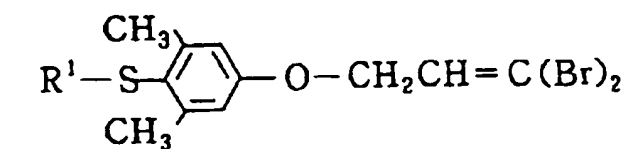
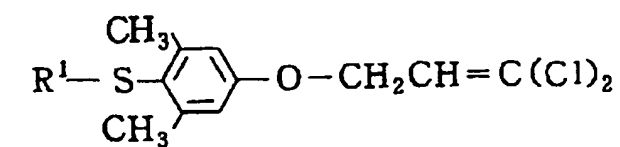
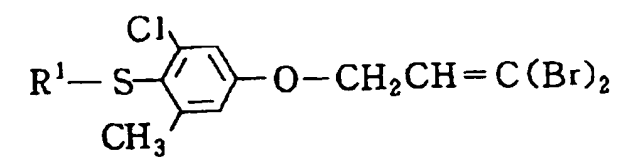
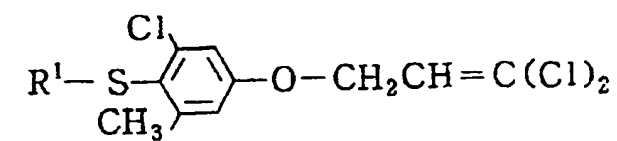
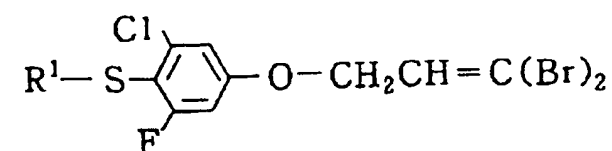
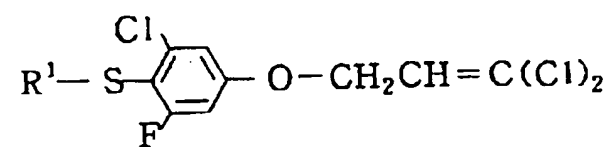
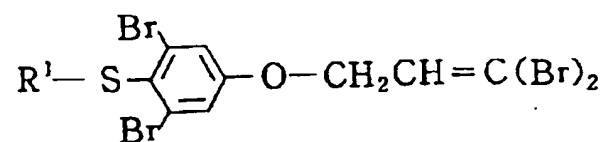
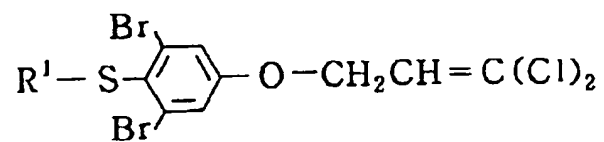


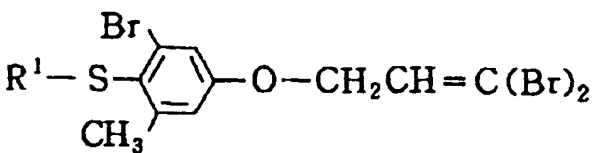
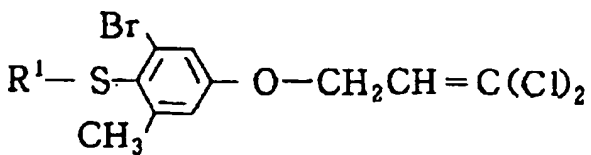
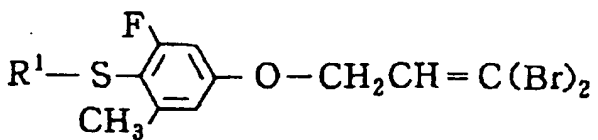
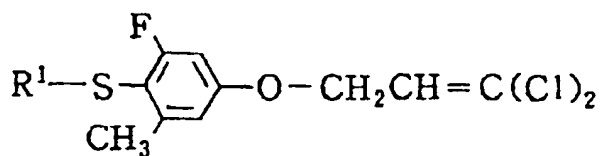
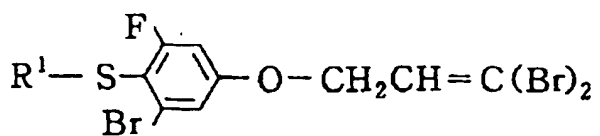
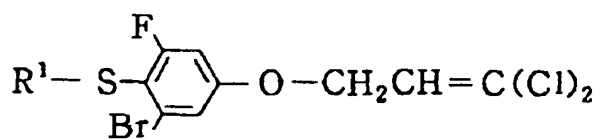
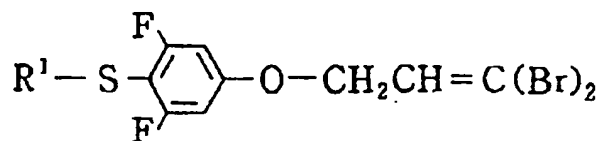
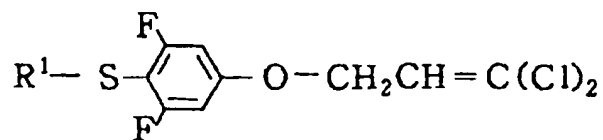
wherein R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , Q^1 , Q^2 , p and l are as defined in Tables 1 to 6 below, $n\text{-C}_3\text{H}_7$ and $n\text{-Pr}$ mean n -propyl, and $\text{iso-C}_3\text{H}_7$ and iso-Pr mean isopropyl.

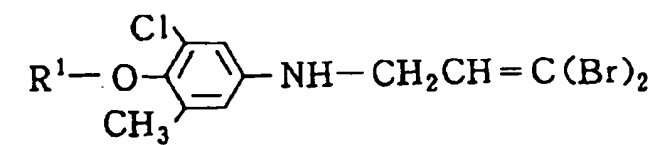
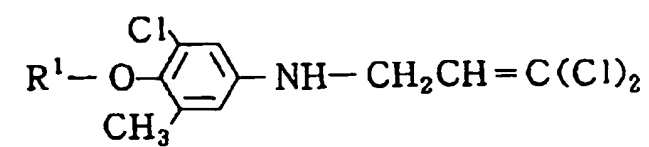
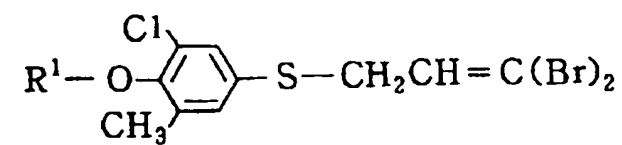
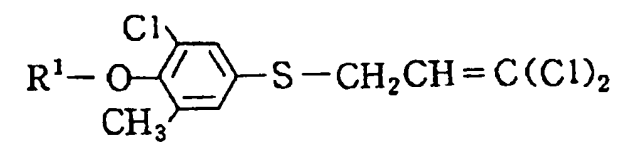
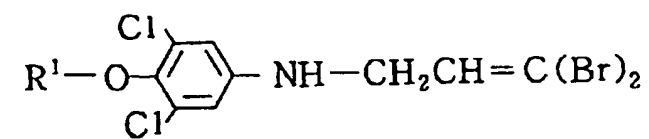
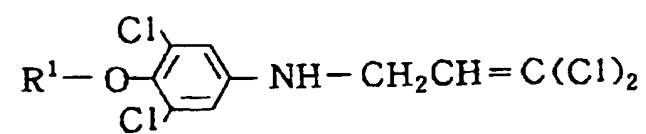
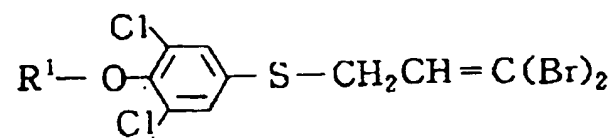
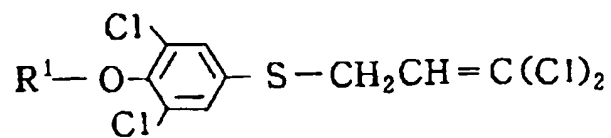


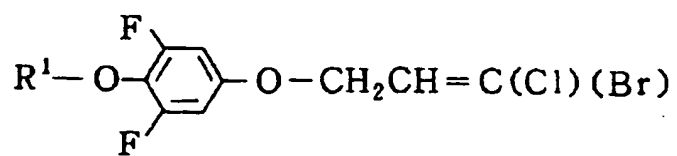
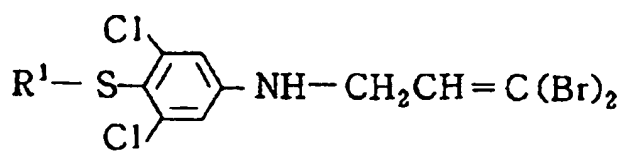
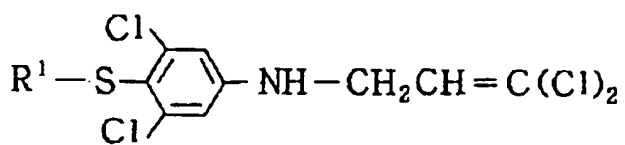
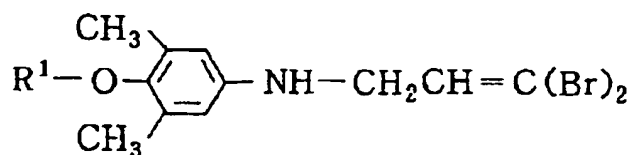
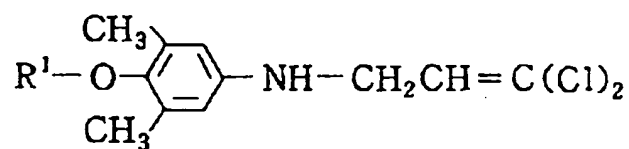
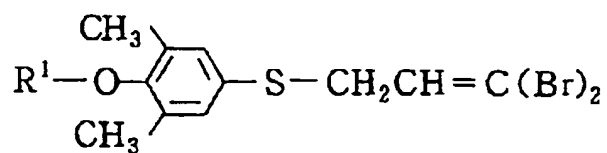
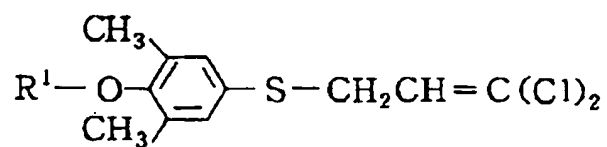


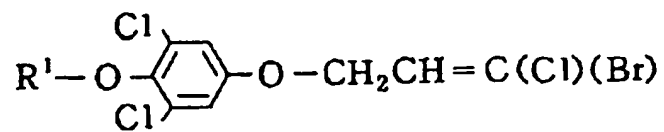
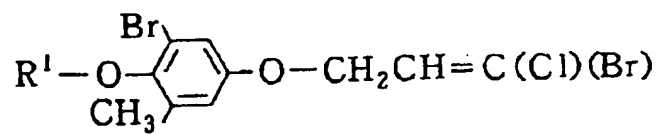
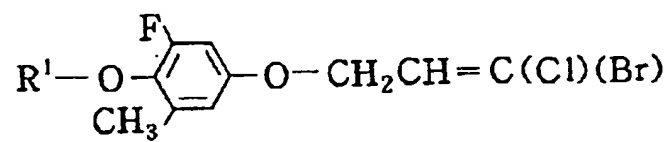
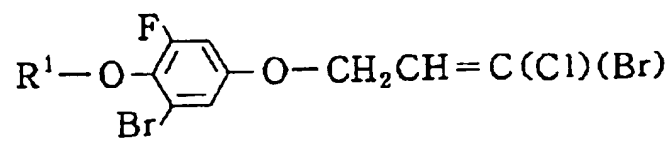


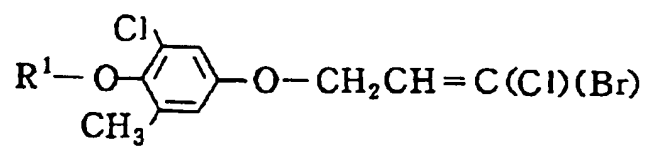
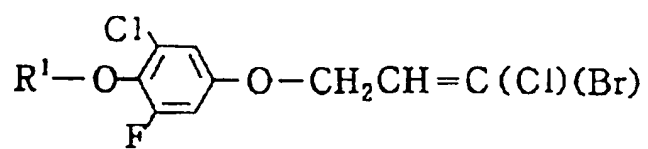
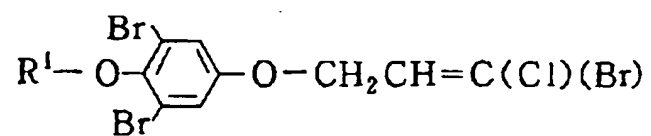
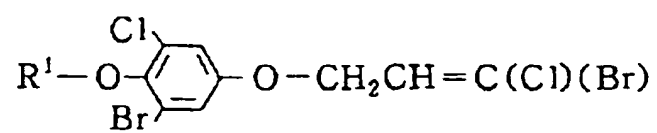


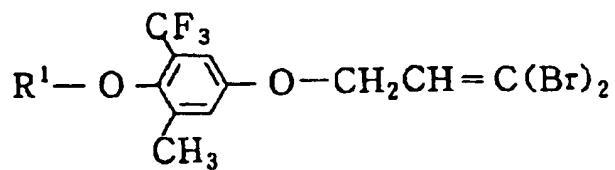
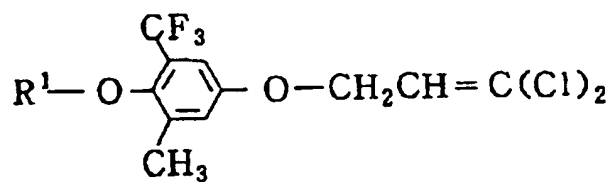
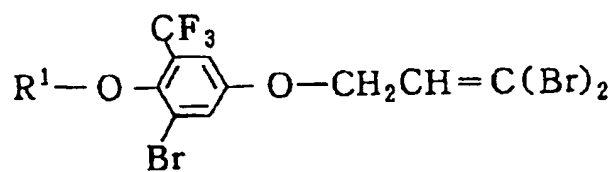
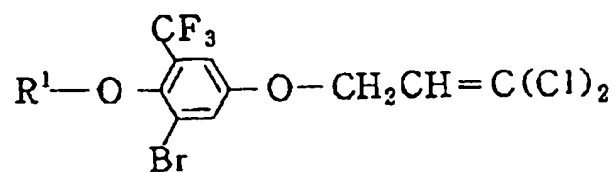
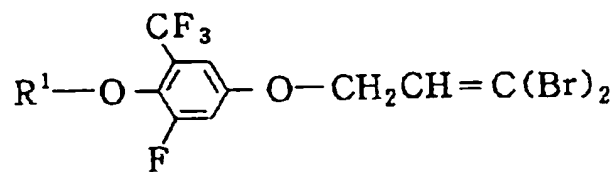
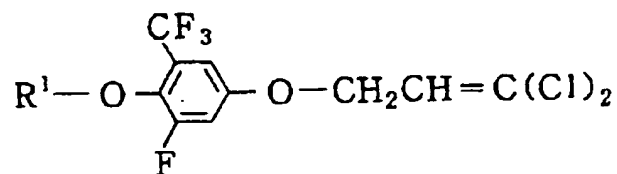
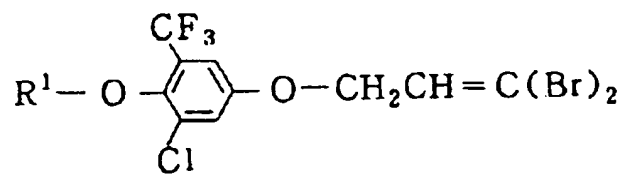
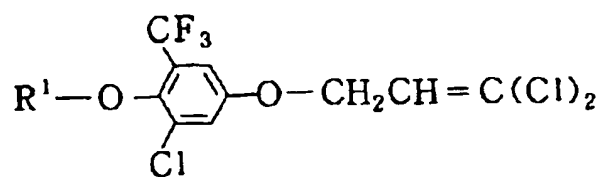


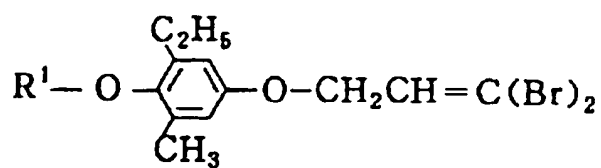
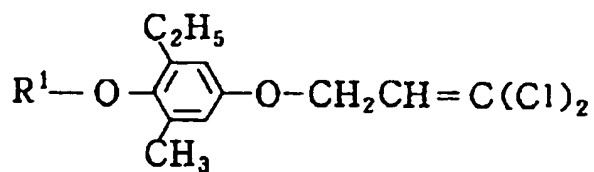
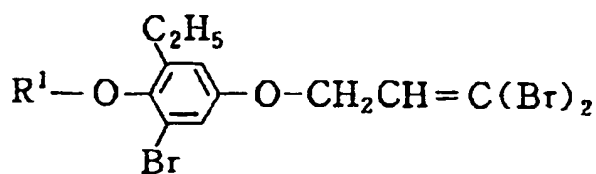
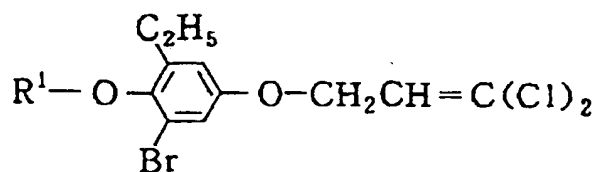
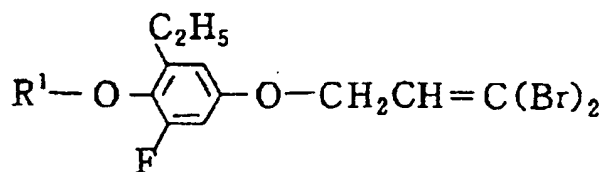
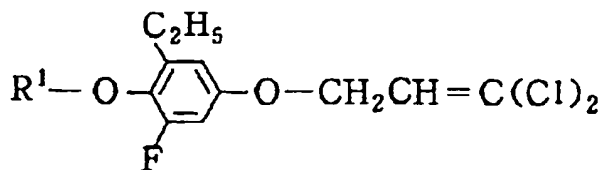
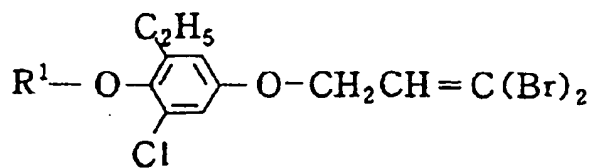
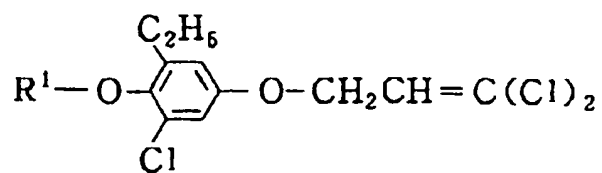


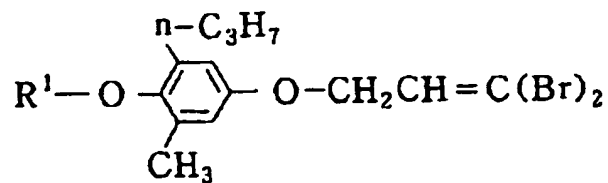
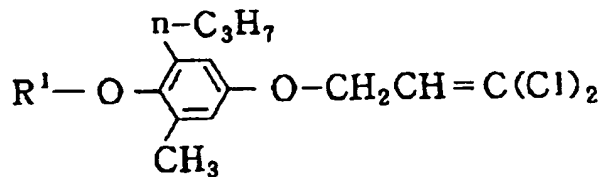
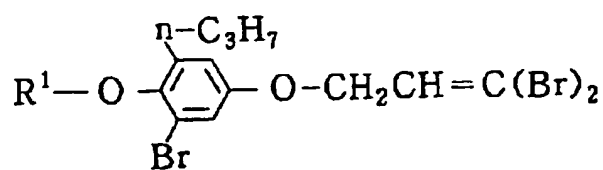
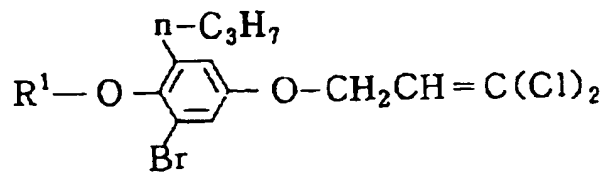
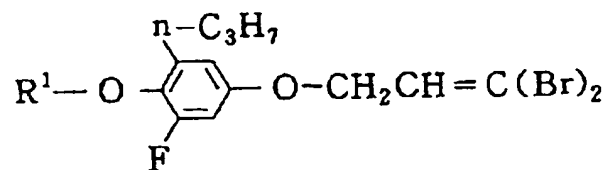
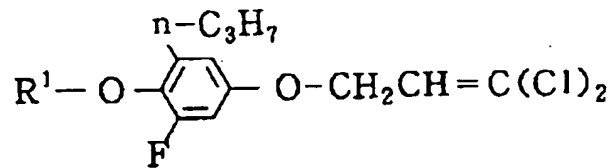
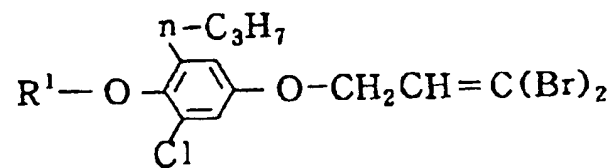
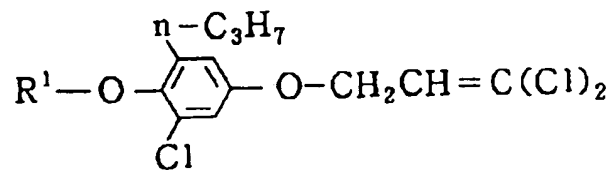


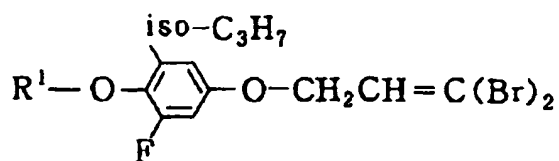
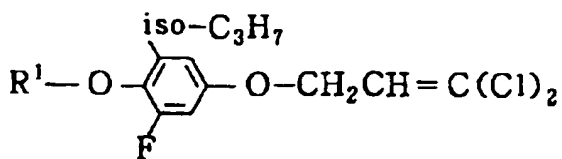
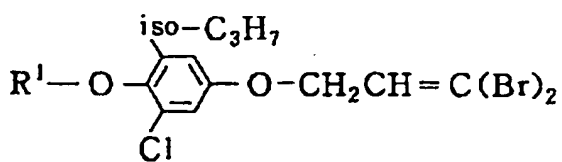
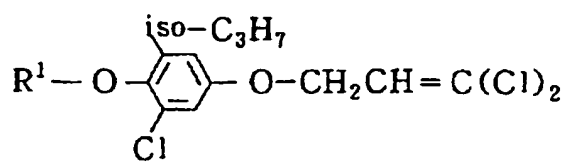
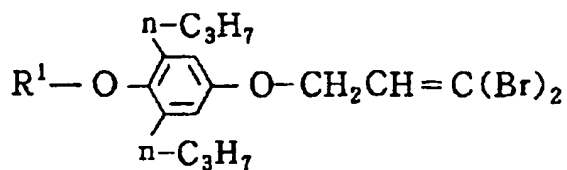
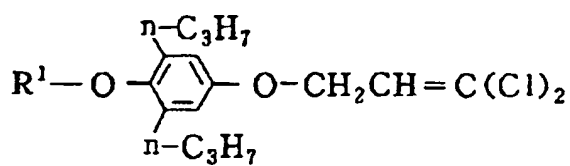
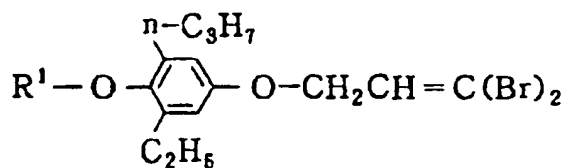
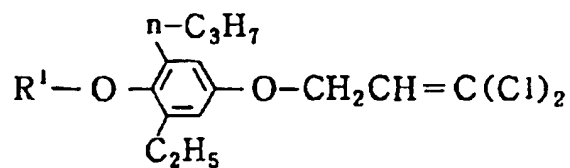


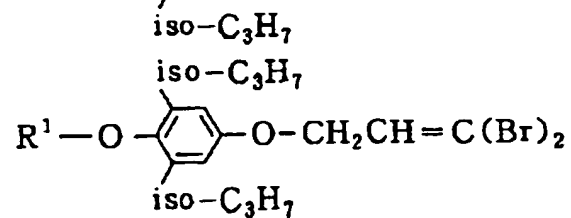
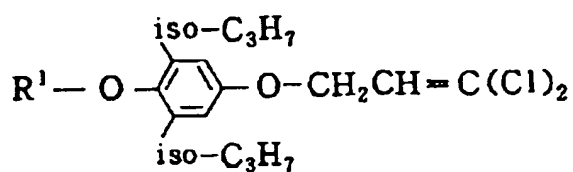
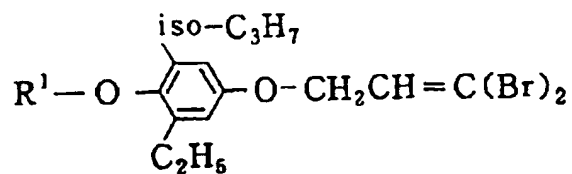
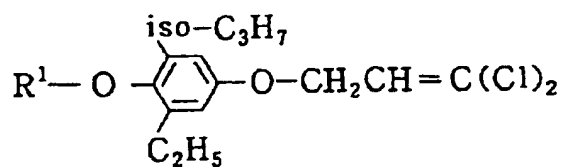
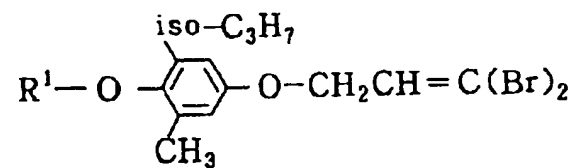
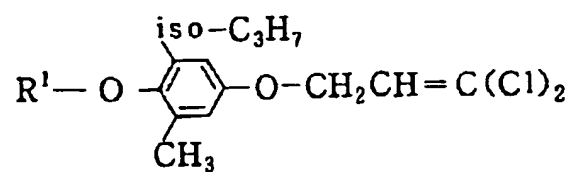
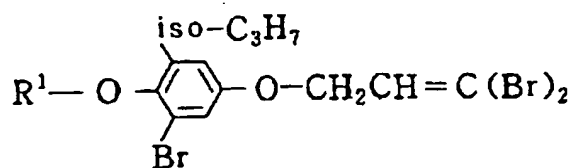
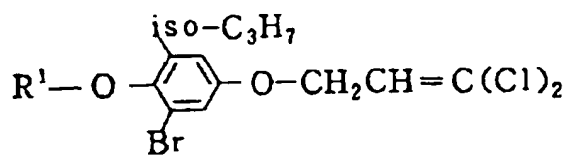


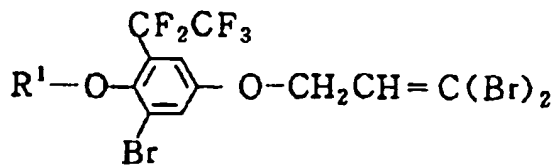
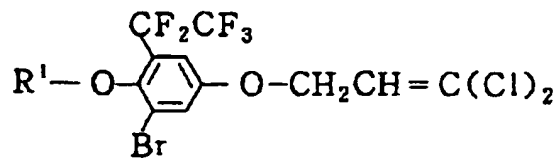
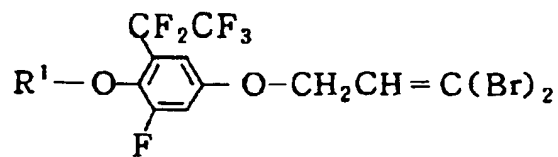
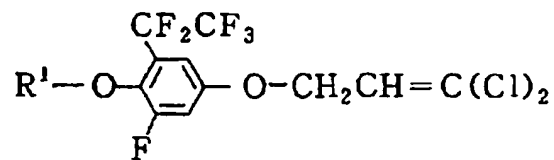
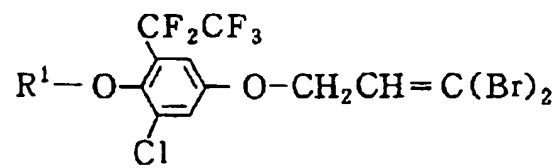
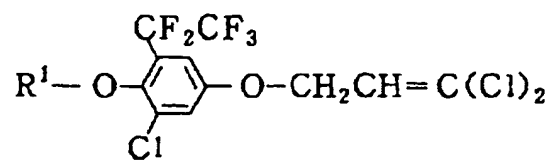
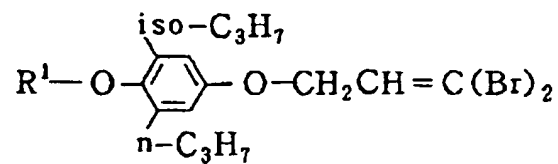
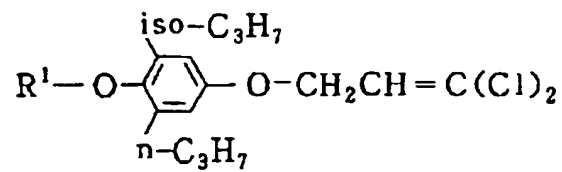


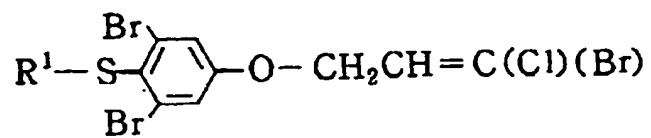
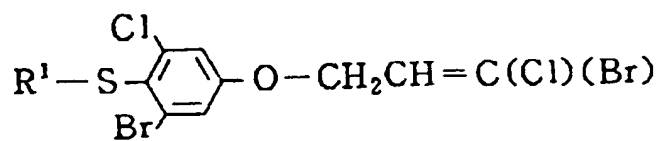
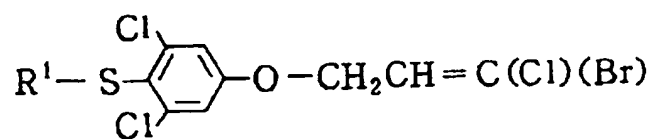
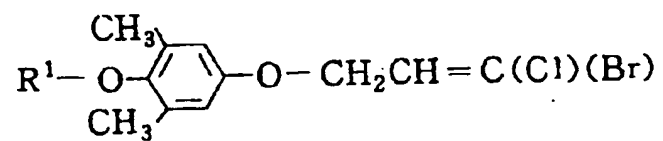


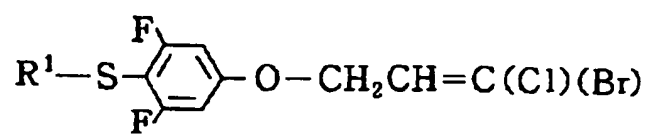
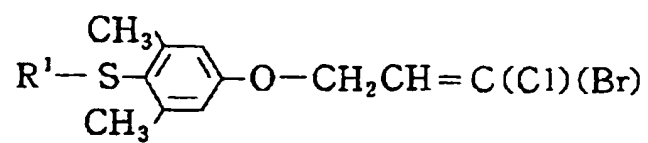
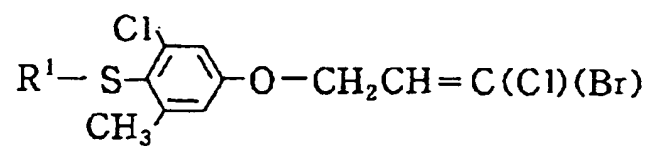
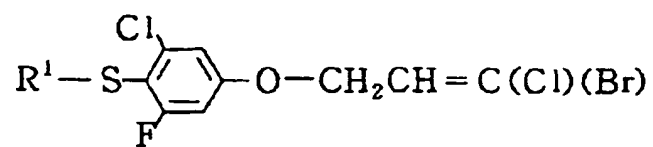


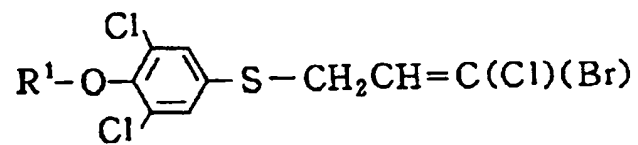
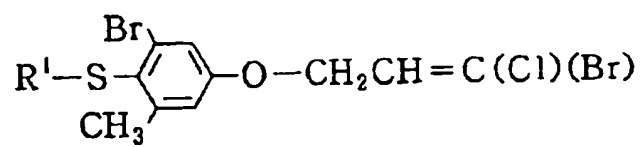
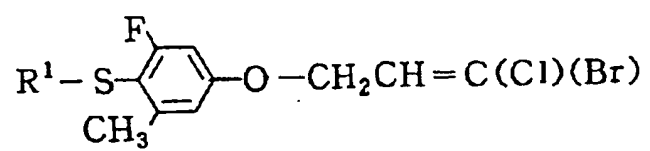
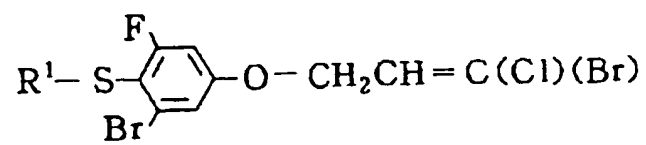


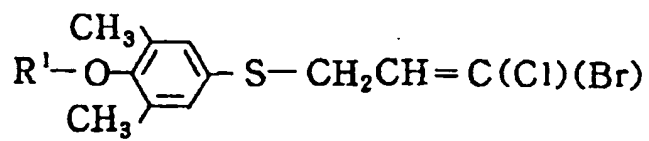
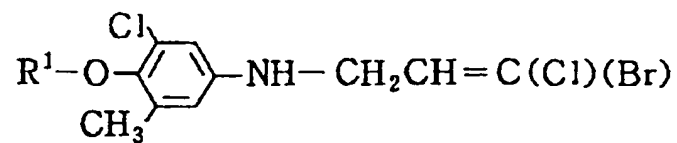
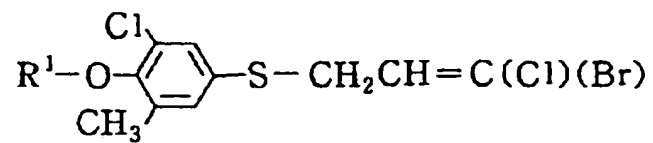
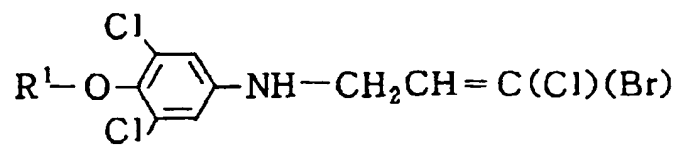


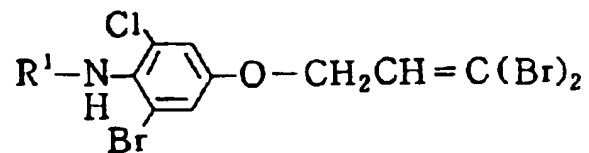
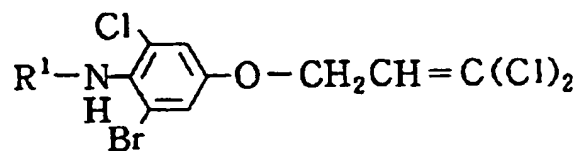
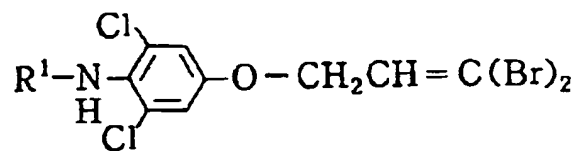
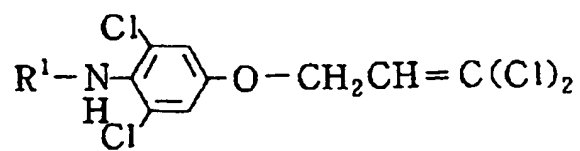
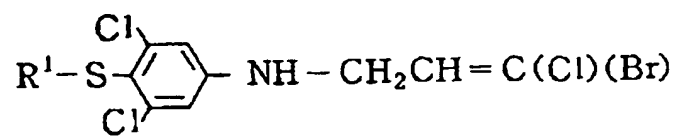
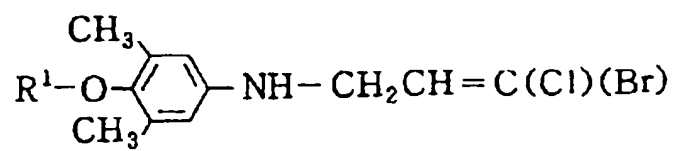


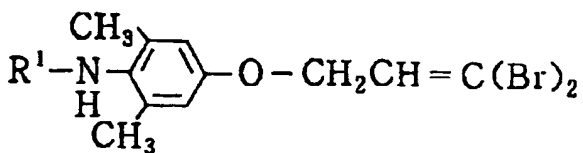
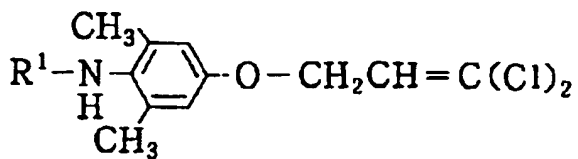
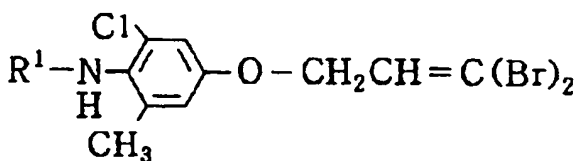
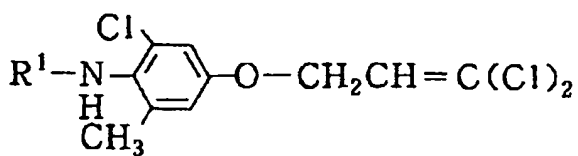
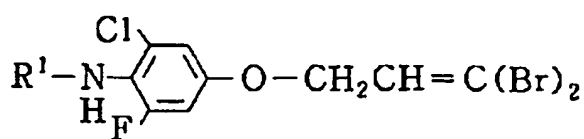
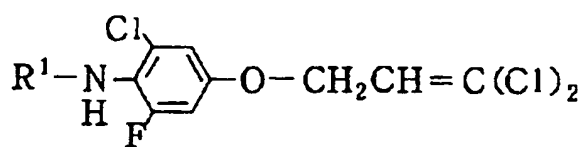
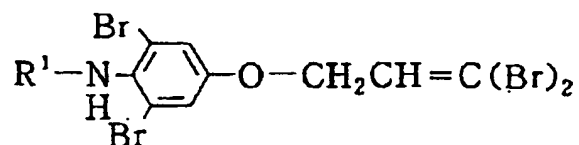
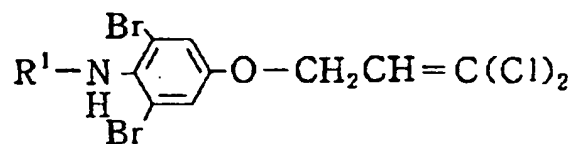


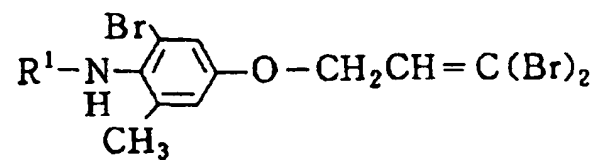
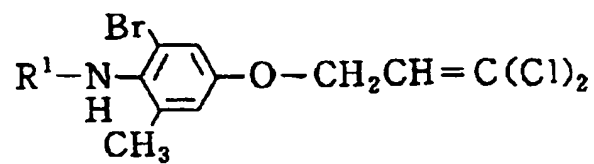
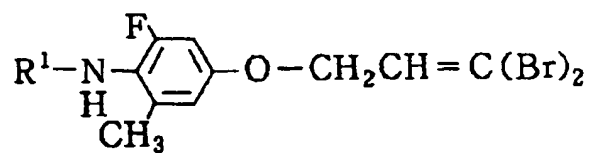
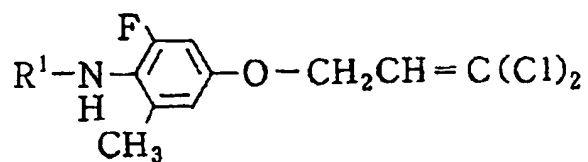
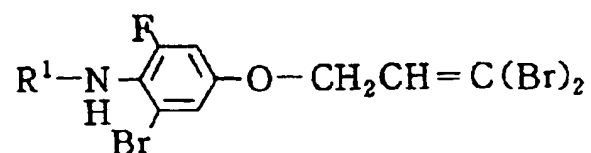
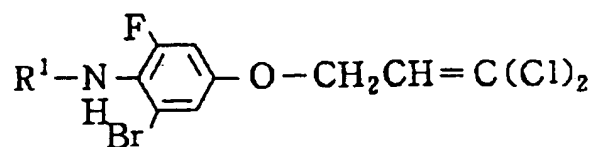
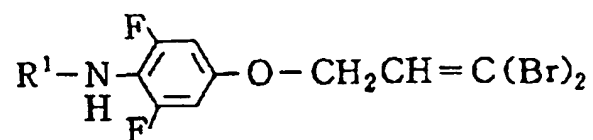
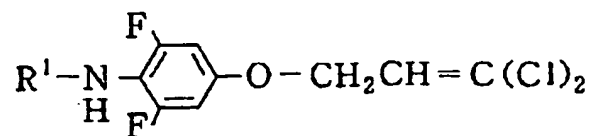


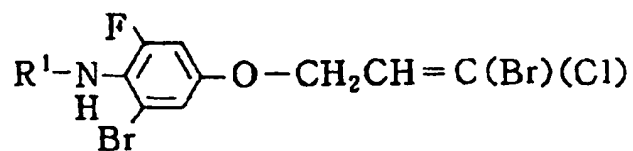
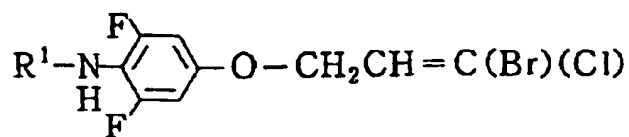
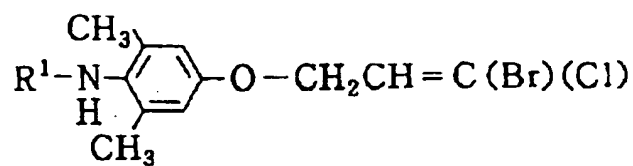
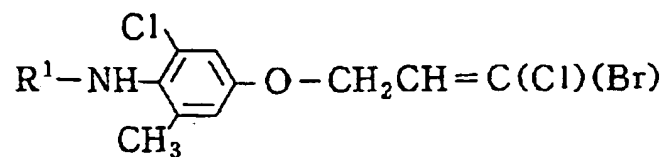
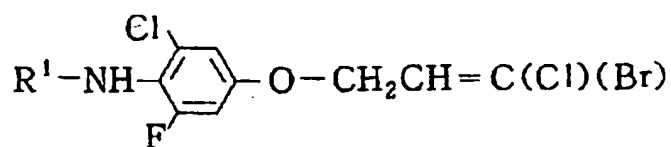
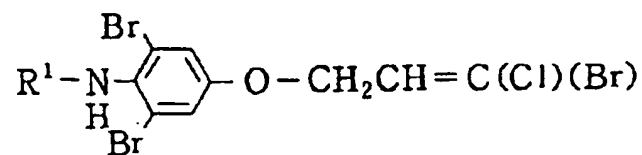
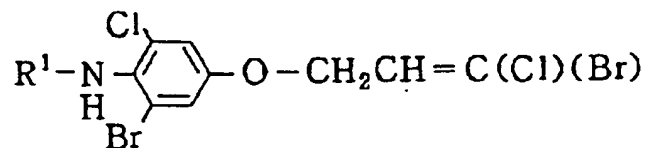
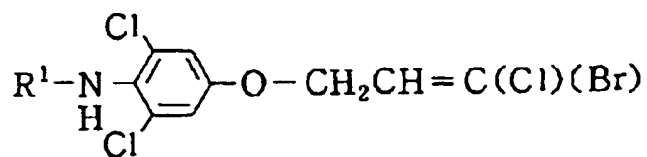


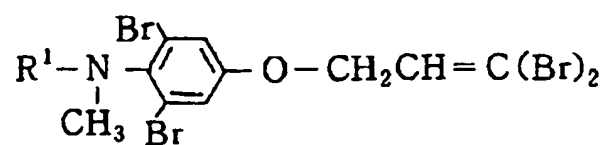
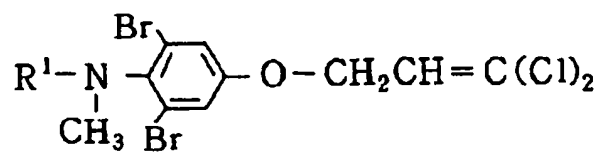
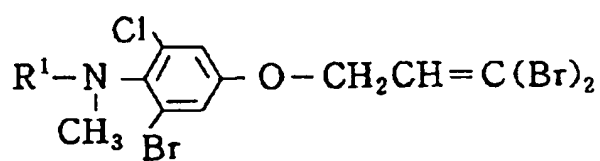
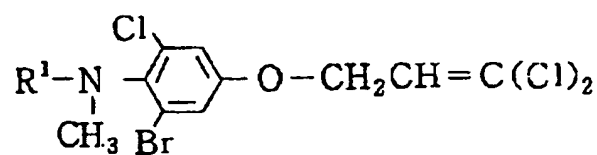
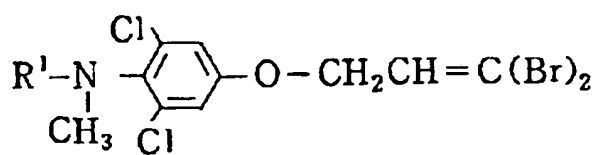
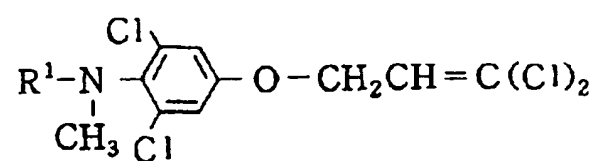
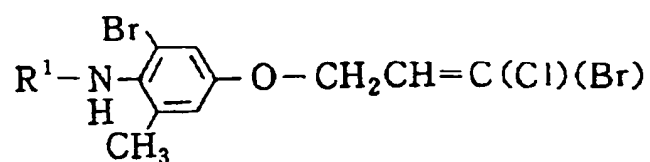
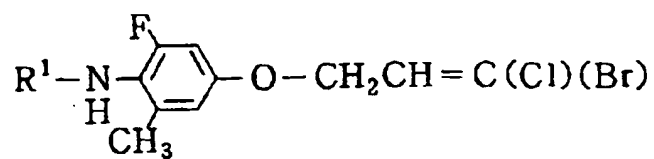


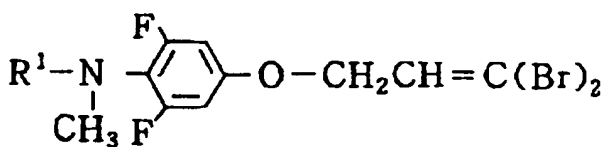
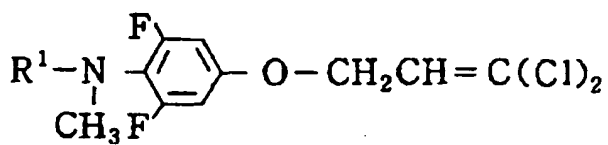
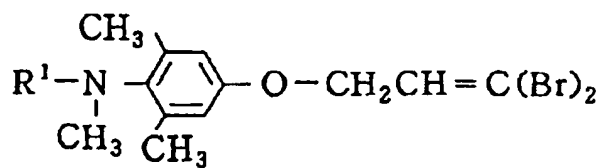
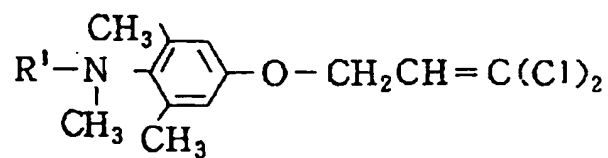
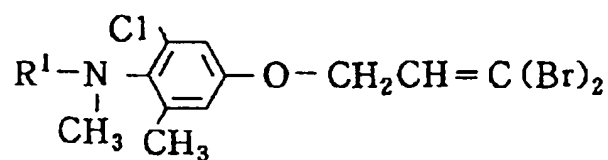
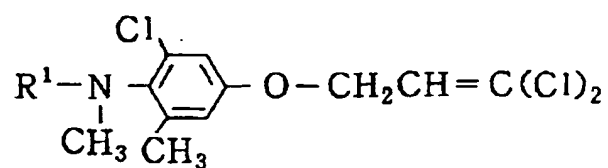
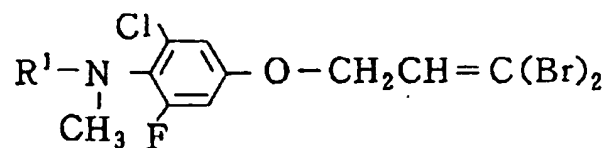
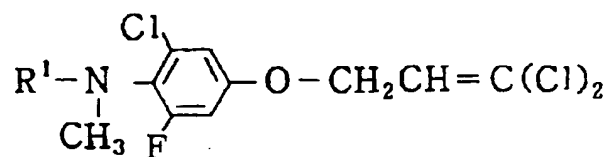


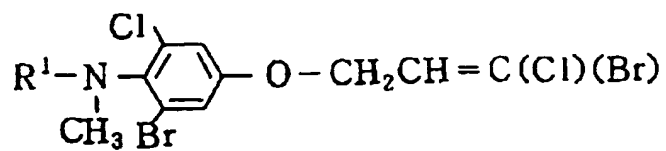
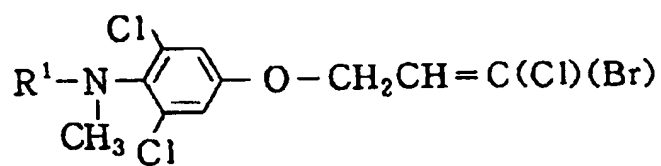
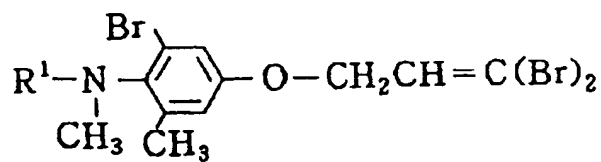
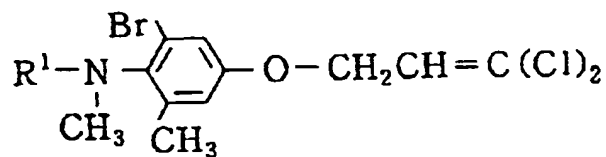
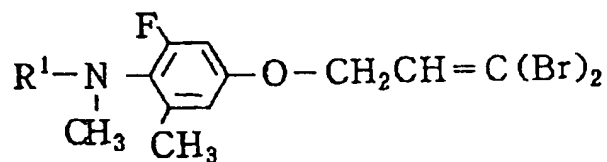
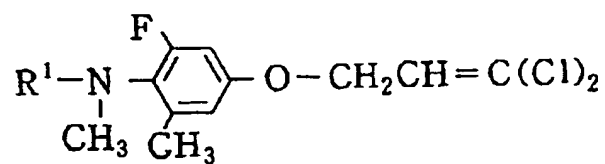
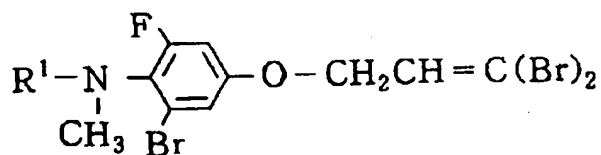
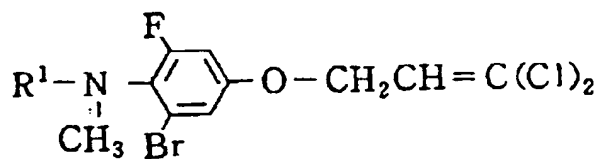


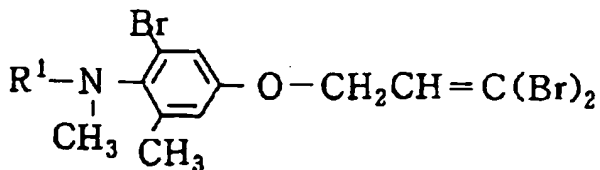
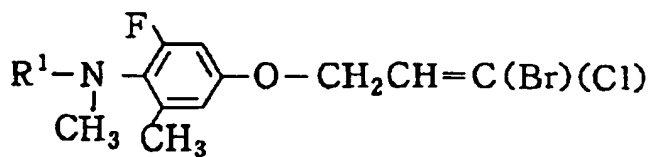
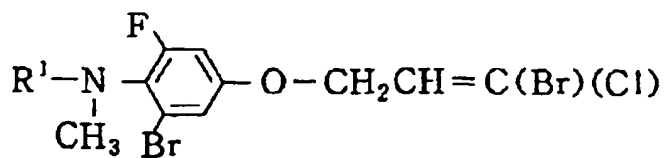
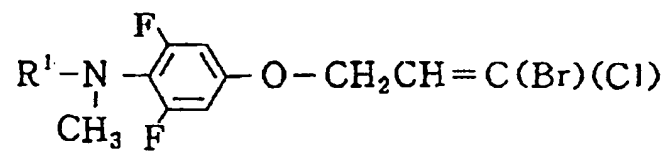
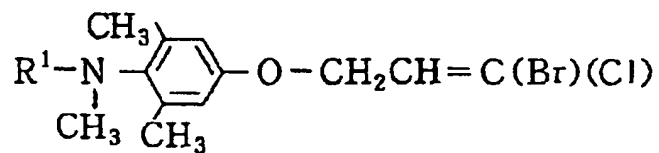
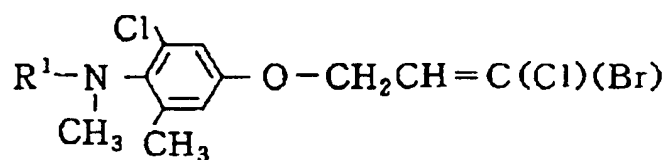
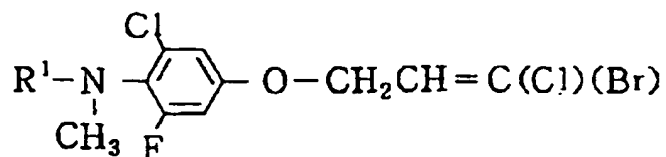
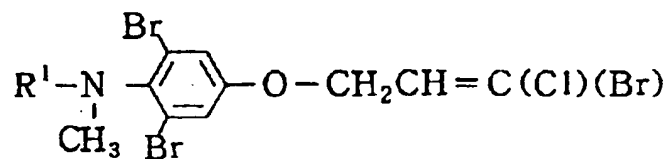


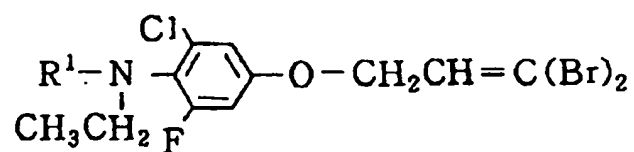
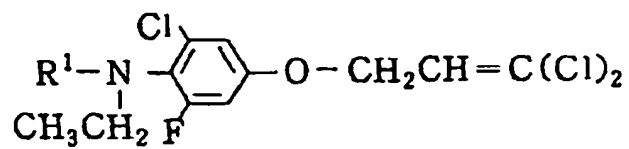
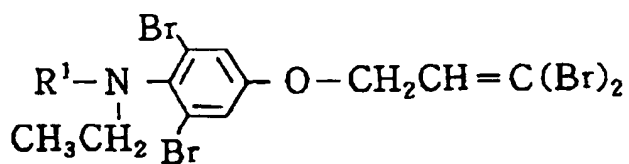
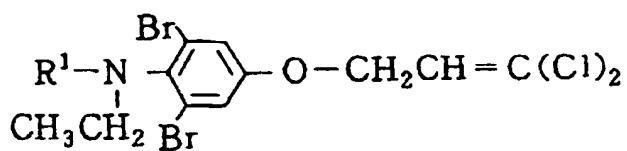
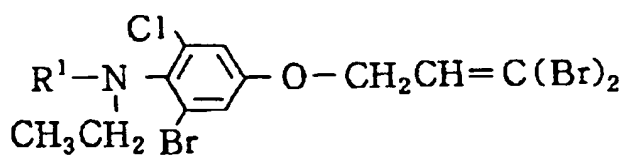
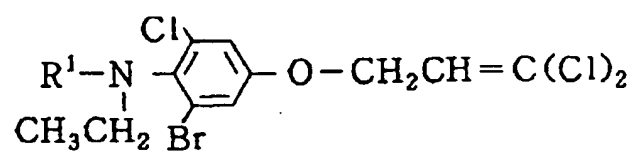
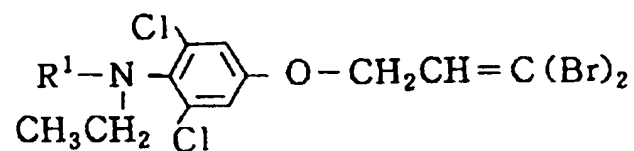
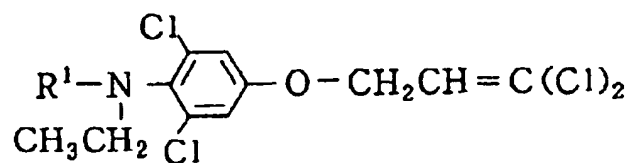


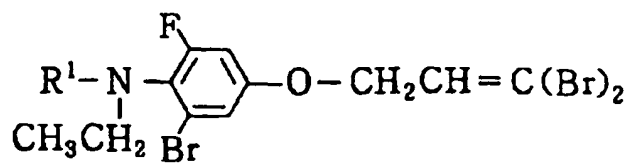
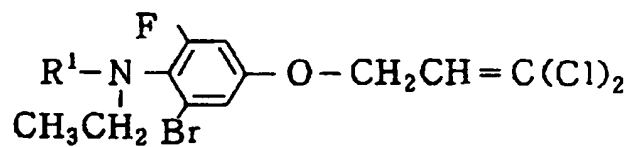
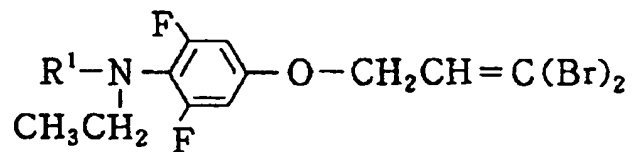
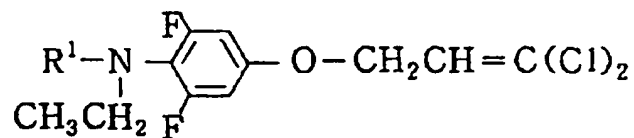
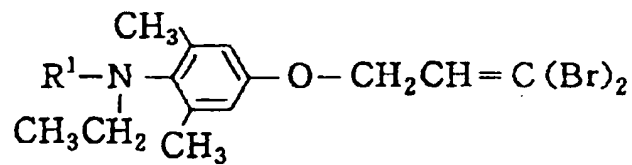
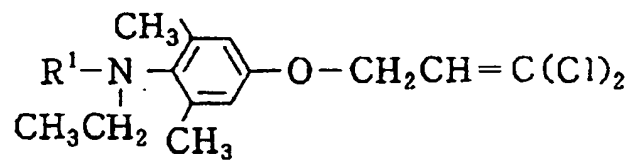
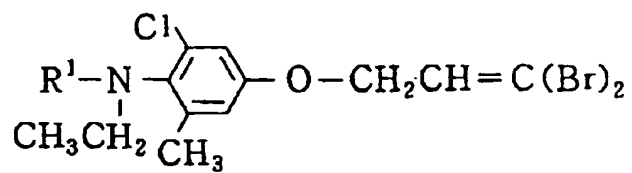
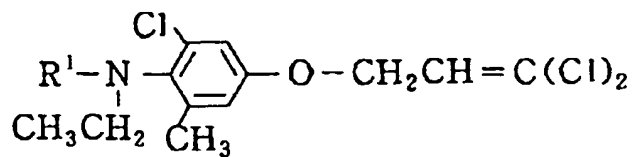


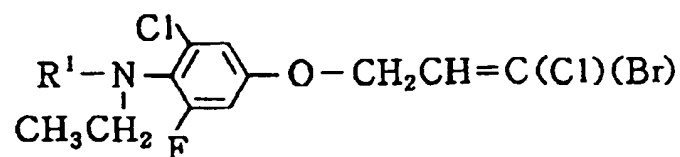
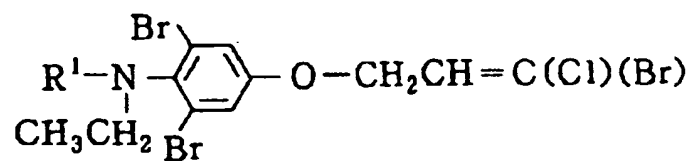
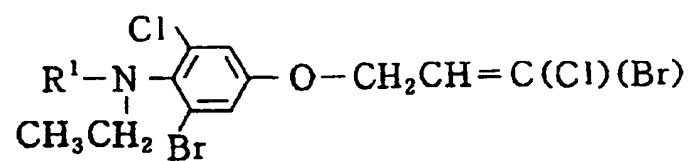
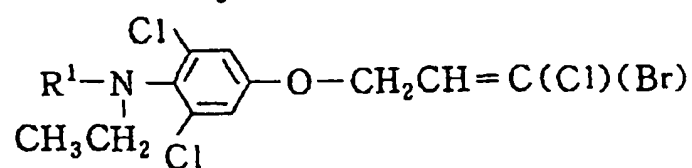
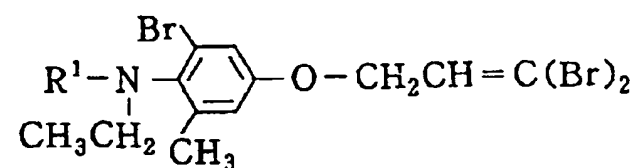
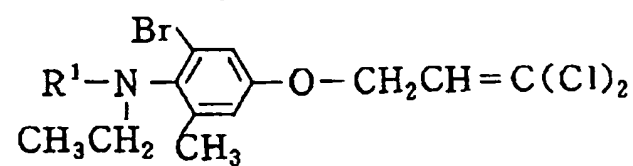
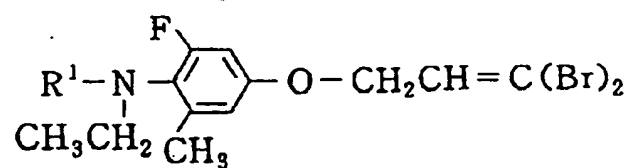
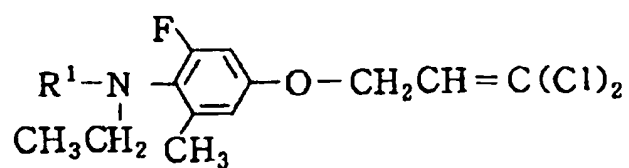


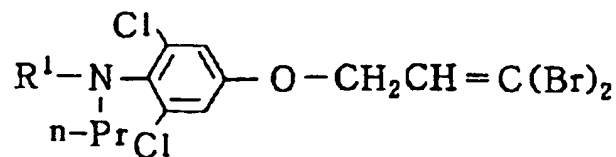
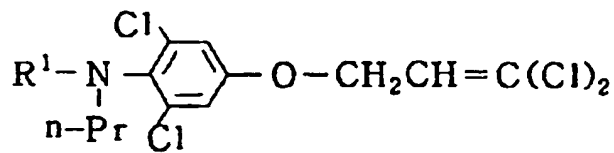
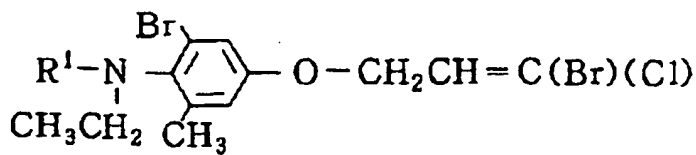
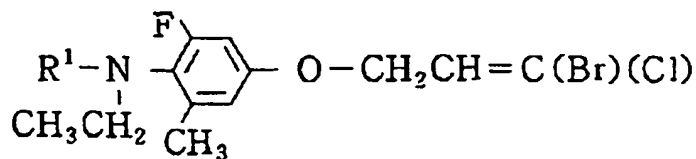
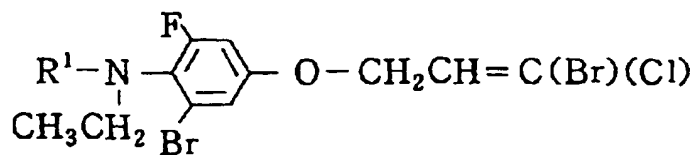
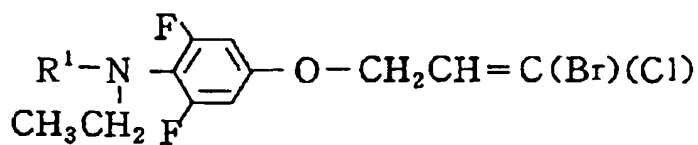
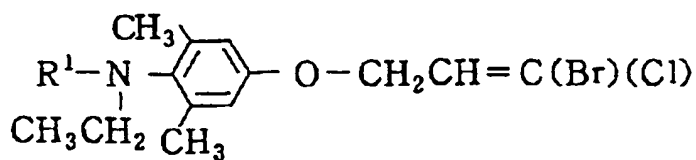
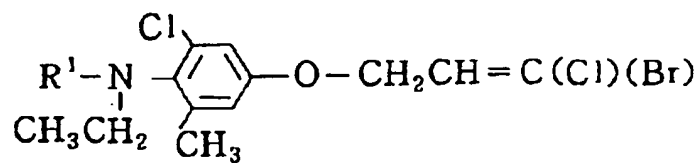


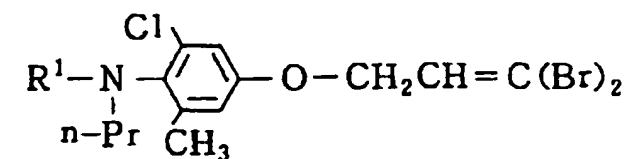
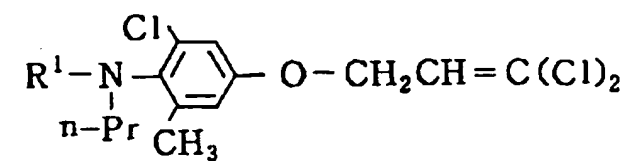
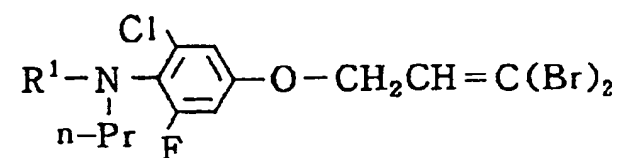
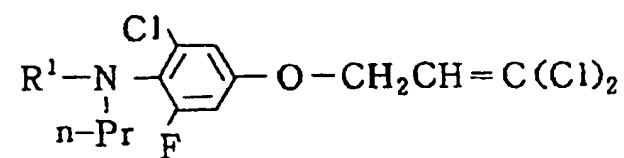
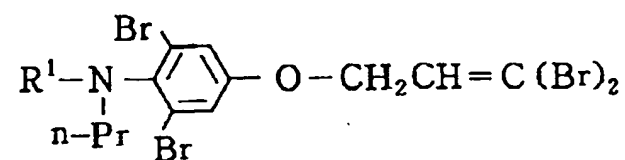
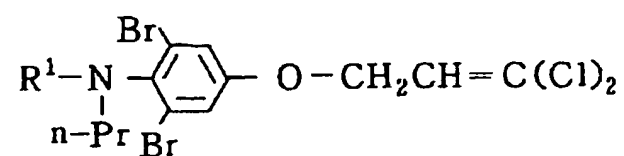
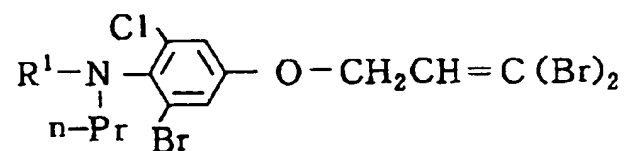
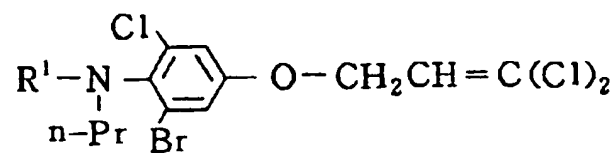


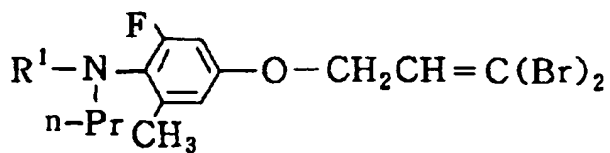
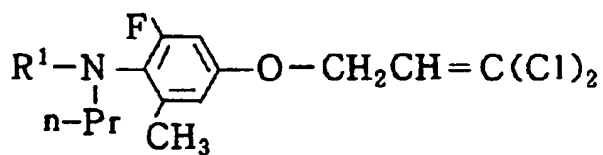
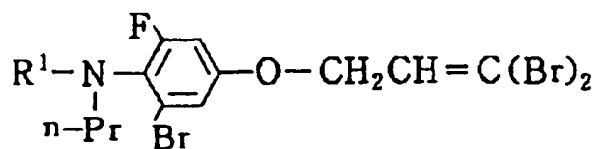
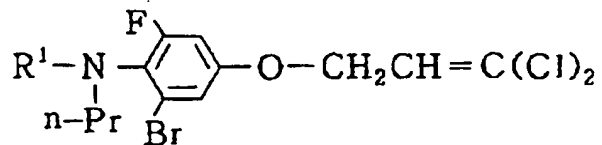
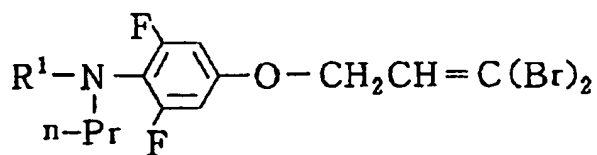
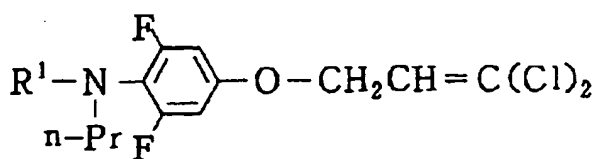
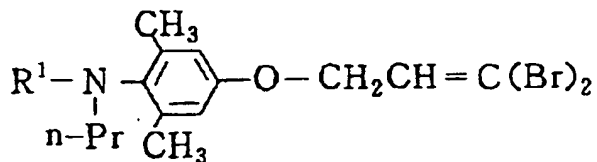
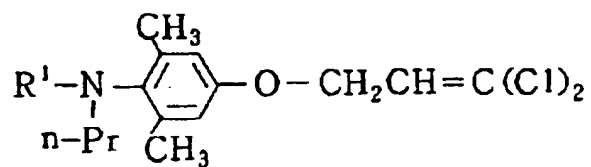


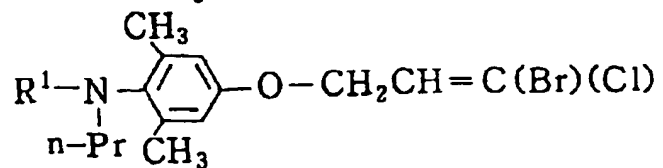
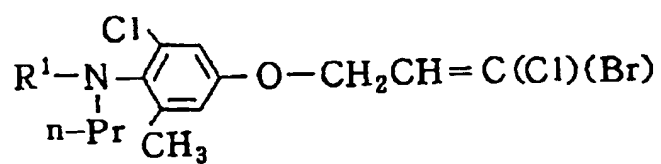
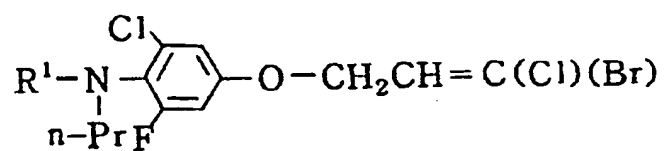
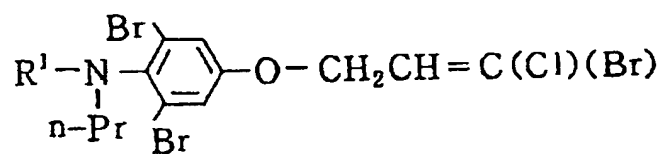
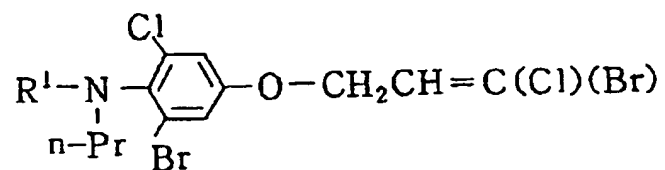
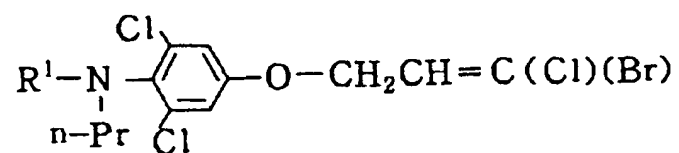
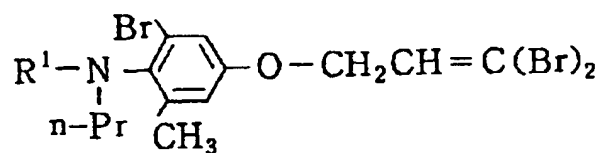
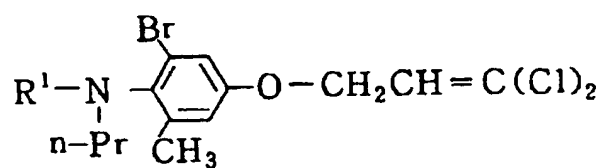


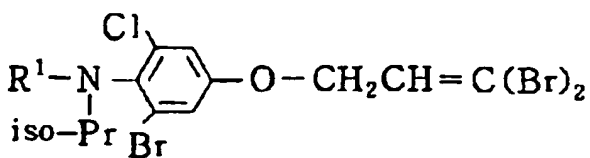
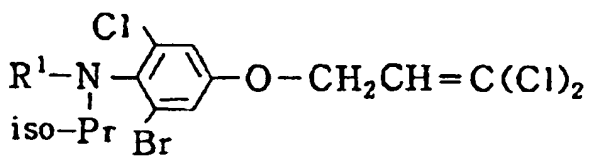
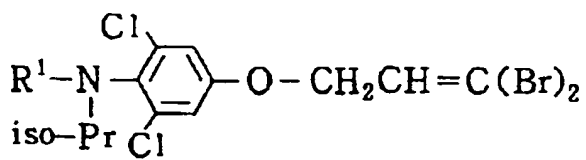
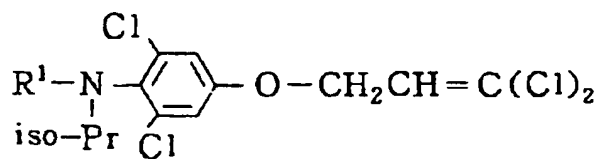
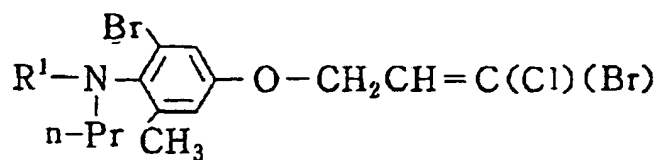
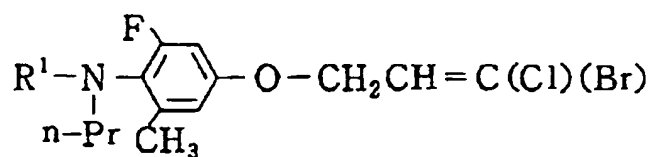
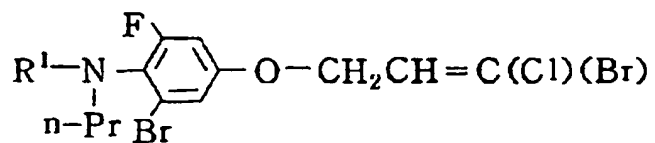
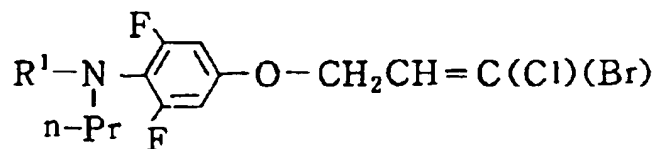


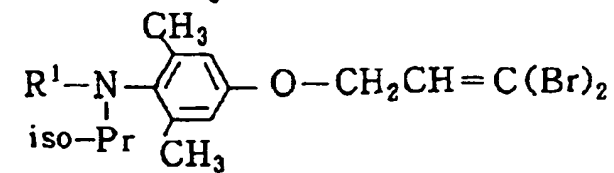
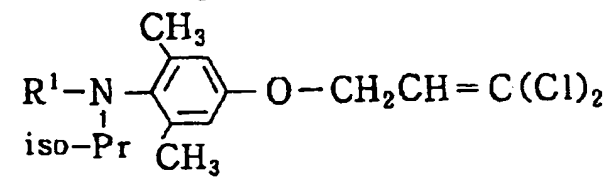
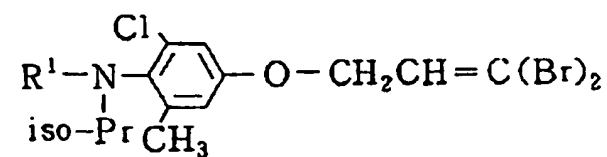
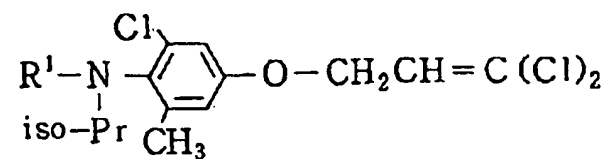
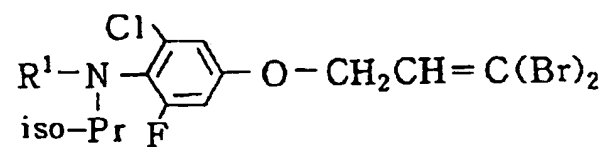
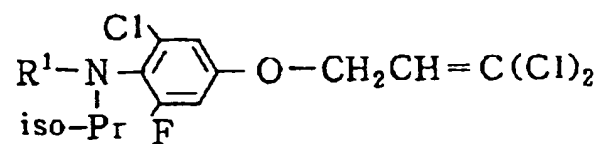
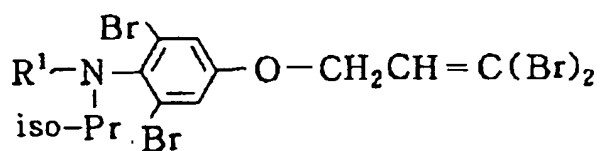
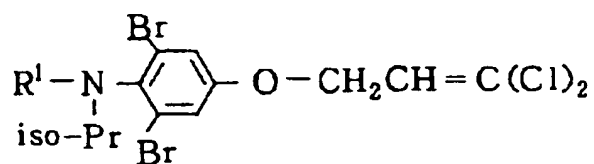


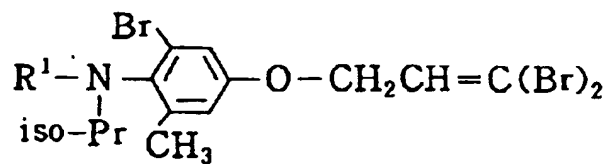
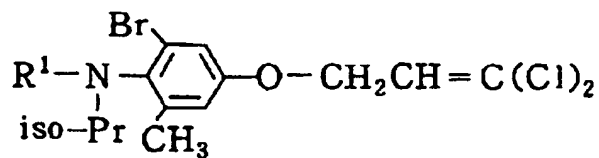
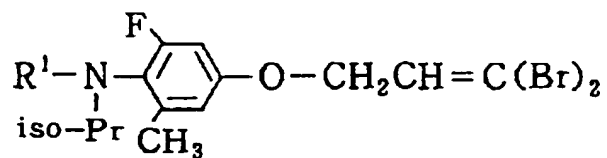
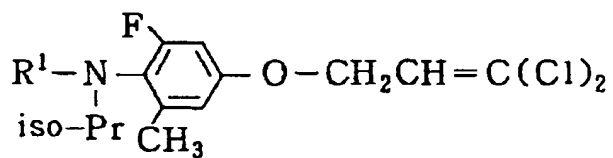
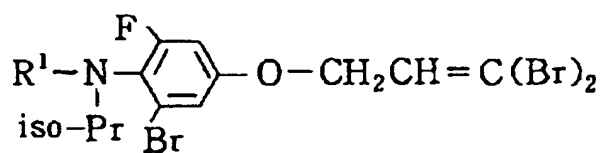
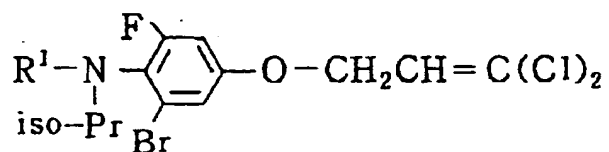
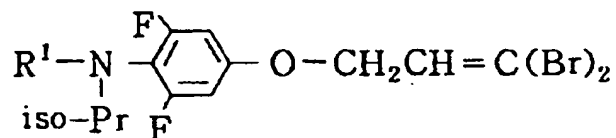
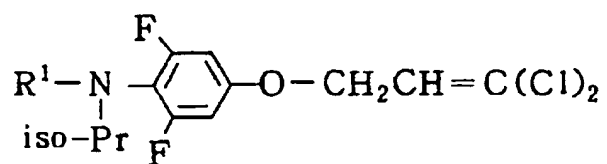


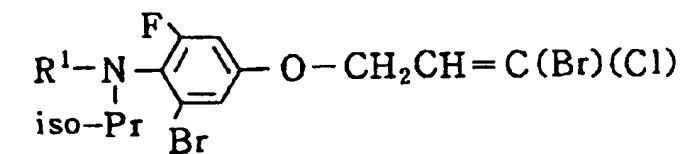
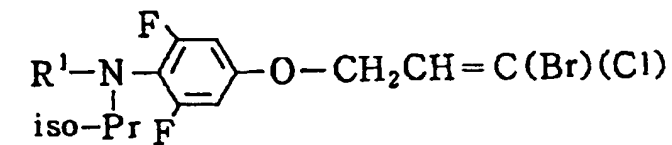
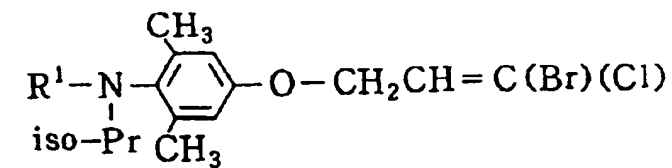
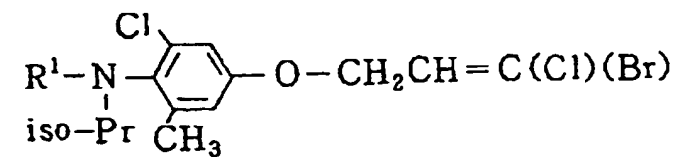
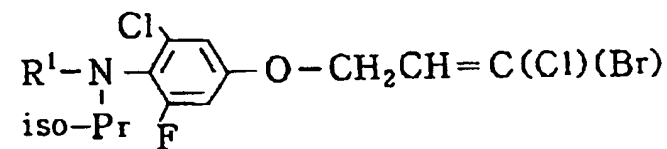
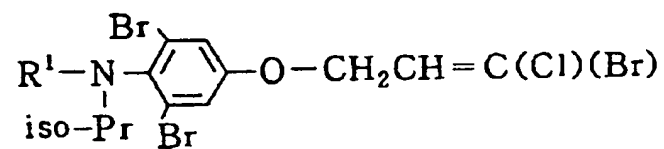
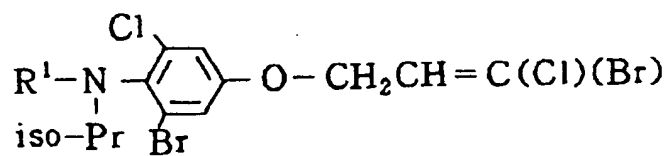
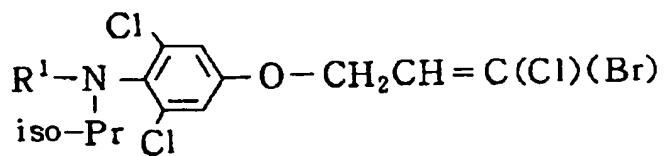


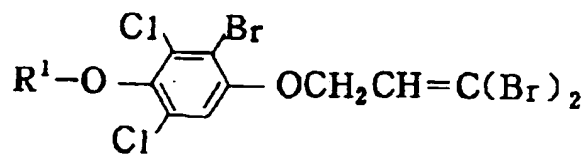
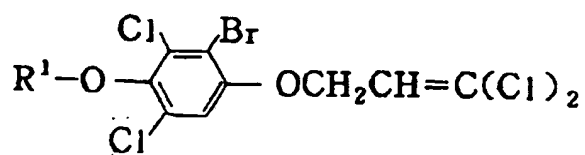
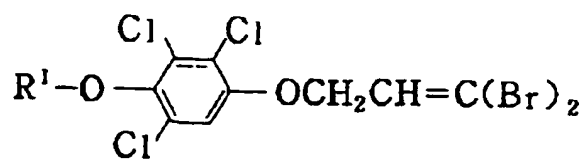
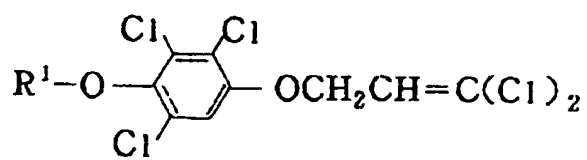
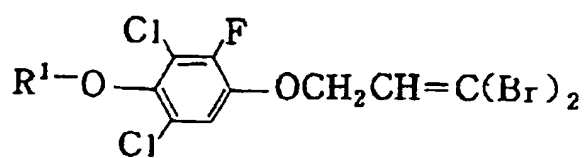
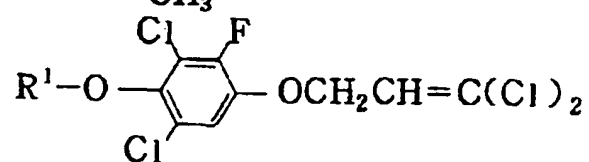
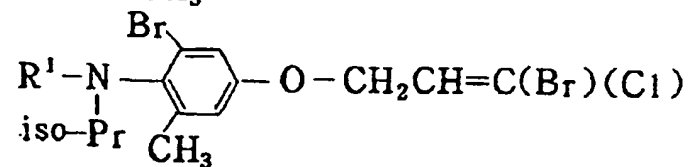
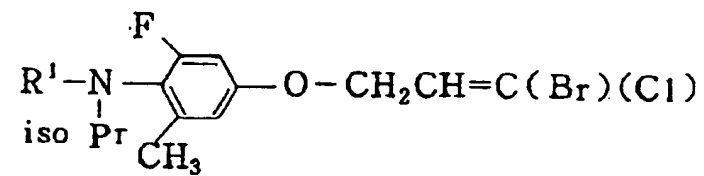


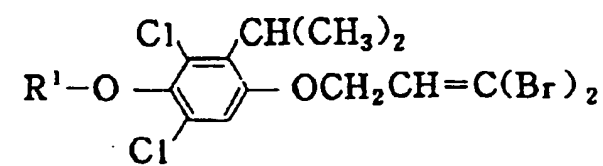
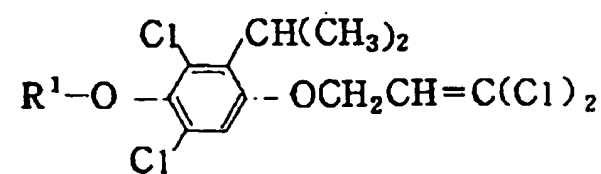
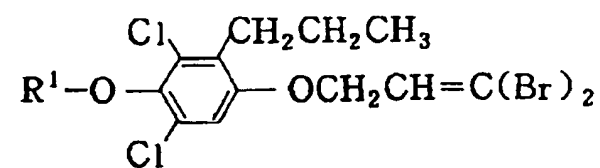
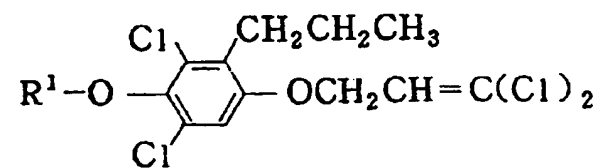
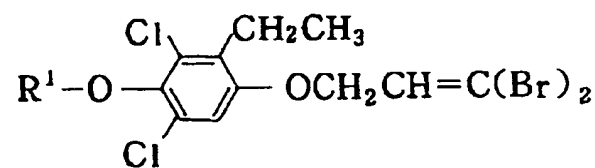
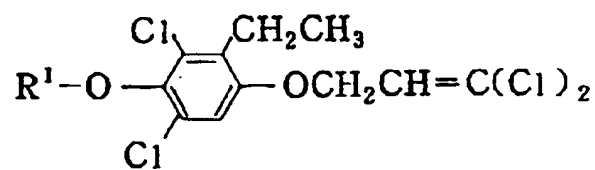
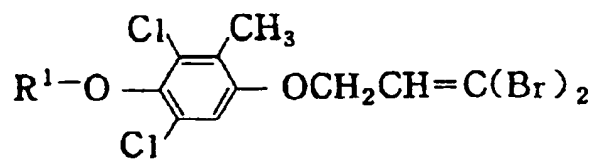
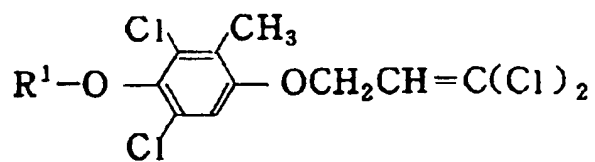


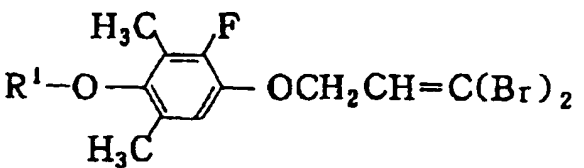
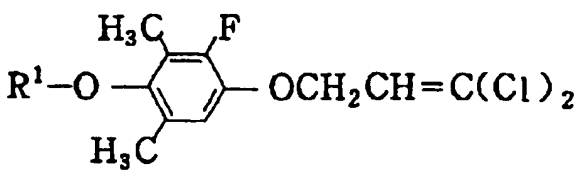
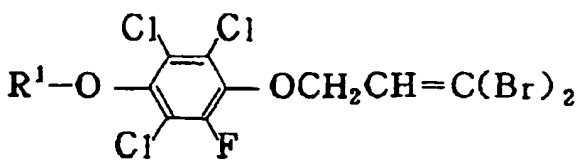
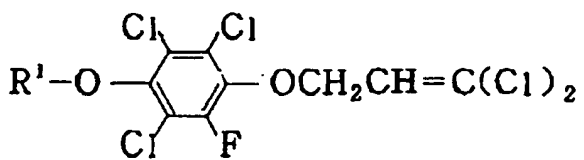
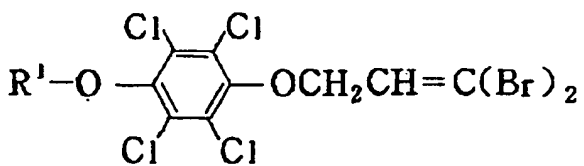
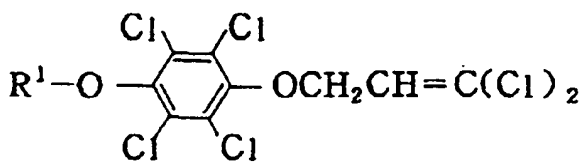
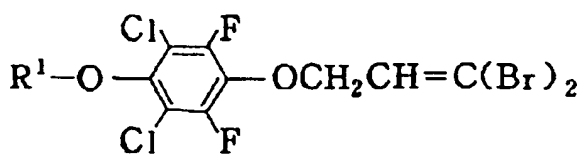
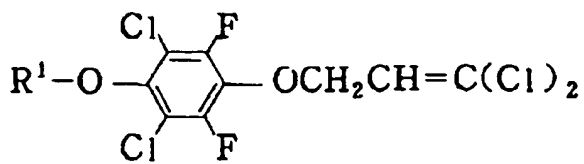


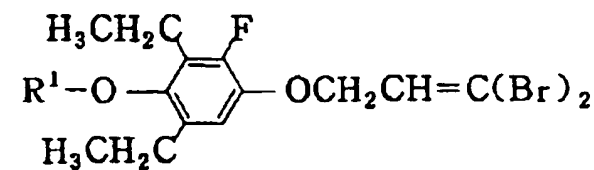
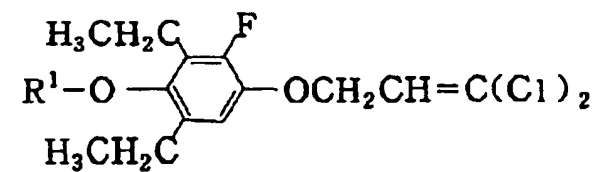
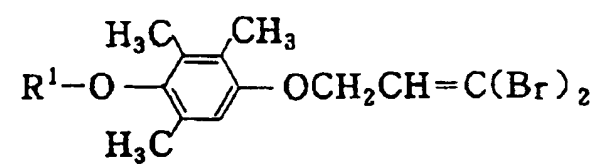
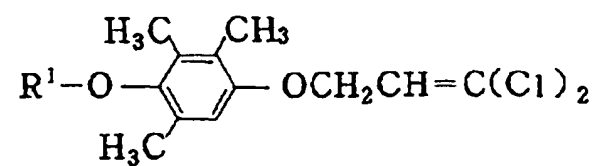
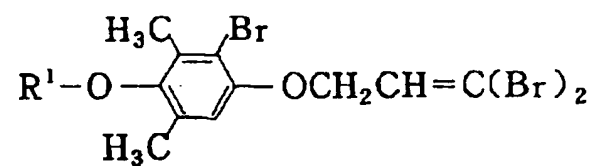
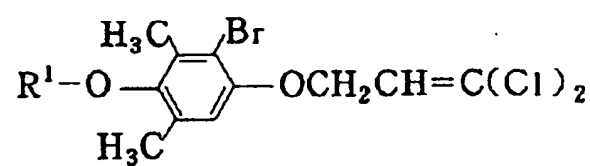
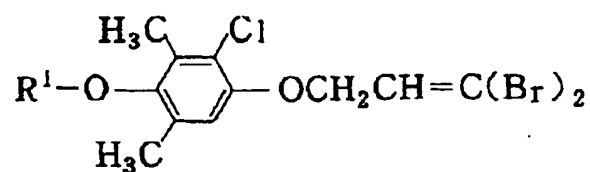
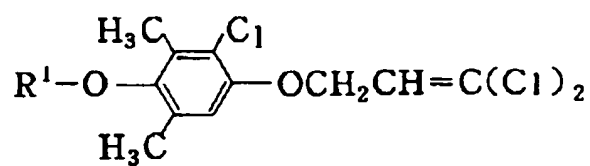


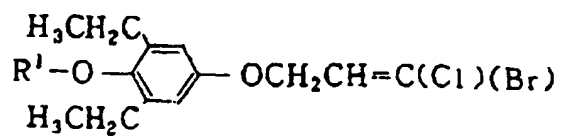
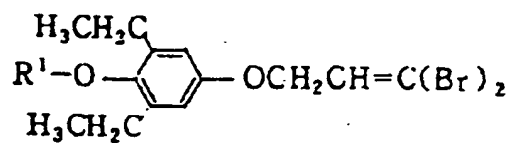
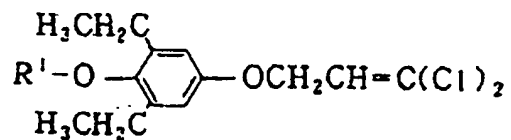
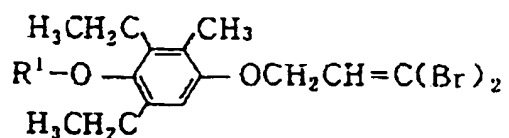
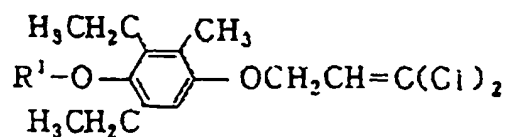
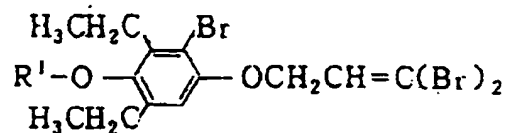
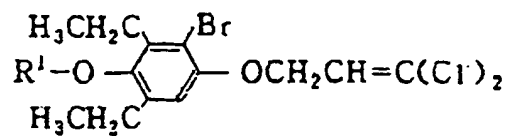
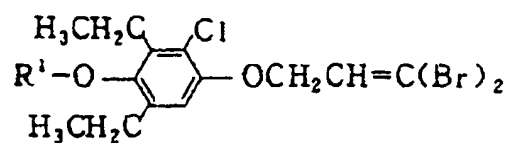
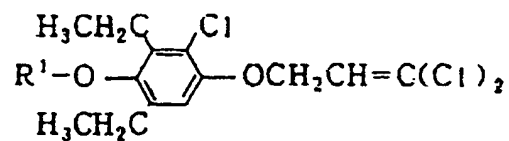
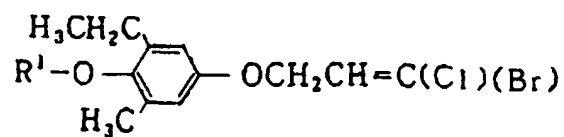


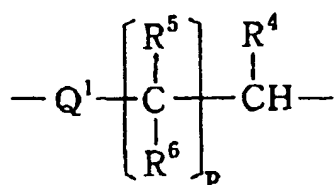










TALBLE 1

- O-CH₂ -
- O- (CH₂)₂ -
- O- (CH₂)₃ -
- O- (CH₂)₄ -
- O- (CH₂)₅ -
- O- (CH₂)₆ -
- O- (CH₂)₇ -
- NH- (CH₂)₂ -
- NH- (CH₂)₃ -
- NH- (CH₂)₄ -
- NH- (CH₂)₅ -
- S- (CH₂)₂ -
- S- (CH₂)₃ -
- S- (CH₂)₄ -
- S- (CH₂)₅ -
- S (O) - (CH₂)₂ -
- S (O) - (CH₂)₃ -
- S (O) - (CH₂)₄ -

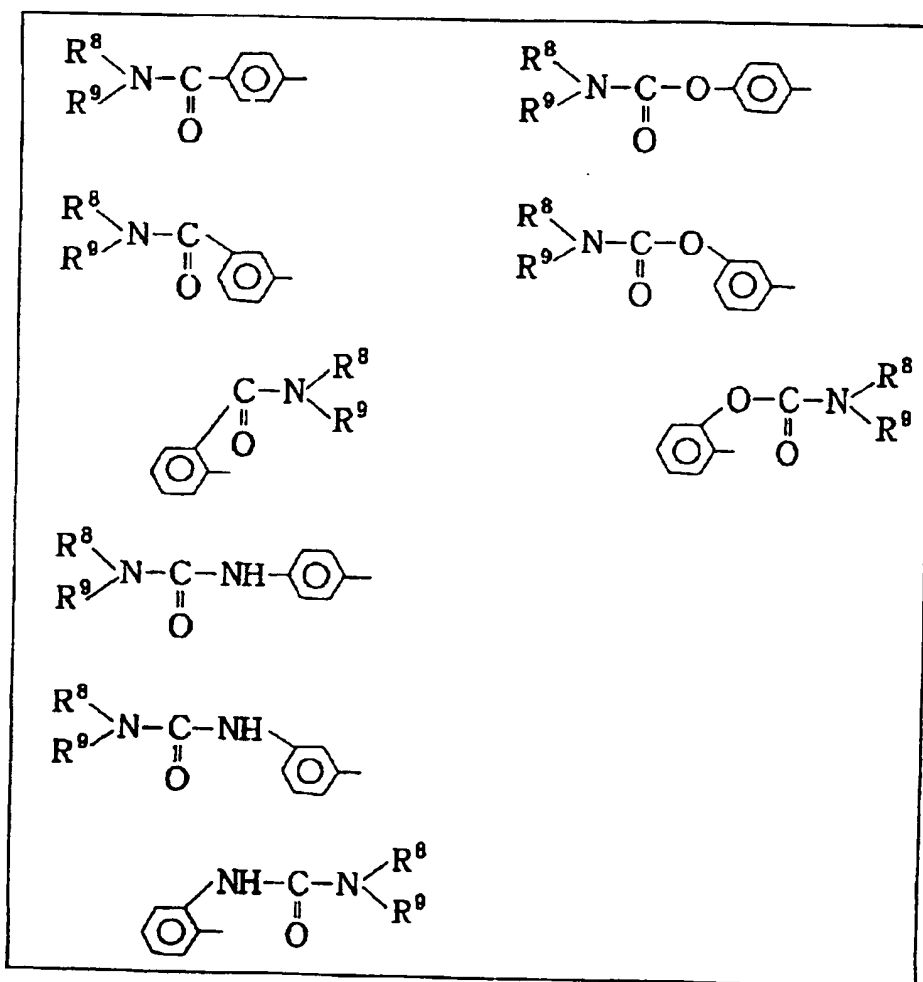
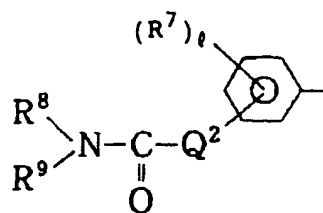
TABLE 1 (contn'd)

$\text{--S (O) -- (CH}_2\text{) }_5\text{ --}$
 $\text{--S (O)}_2\text{ -- (CH}_2\text{) }_2\text{ --}$
 $\text{--S (O)}_2\text{ -- (CH}_2\text{) }_3\text{ --}$
 $\text{--S (O)}_2\text{ -- (CH}_2\text{) }_4\text{ --}$
 $\text{--S (O)}_2\text{ -- (CH}_2\text{) }_5\text{ --}$
 $\text{--O--C (=O) -- (CH}_2\text{) }_2\text{ --}$
 $\text{--O--C (=O) -- (CH}_2\text{) }_3\text{ --}$
 $\text{--O--C (=O) -- (CH}_2\text{) }_4\text{ --}$
 $\text{--O--C (=O) -- (CH}_2\text{) }_5\text{ --}$
 $\text{--NH--C (=O) -- (CH}_2\text{) }_2\text{ --}$
 $\text{--NH--C (=O) -- (CH}_2\text{) }_3\text{ --}$
 $\text{--NH--C (=O) -- (CH}_2\text{) }_4\text{ --}$
 $\text{--NH--C (=O) -- (CH}_2\text{) }_5\text{ --}$
 $\text{--CH}_2\text{ --O-- (CH}_2\text{) }_2\text{ --}$
 $\text{--CH}_2\text{ --O-- (CH}_2\text{) }_3\text{ --}$
 $\text{--CH}_2\text{ --O-- (CH}_2\text{) }_4\text{ --}$
 $\text{--CH}_2\text{ --O-- (CH}_2\text{) }_5\text{ --}$
 $\text{--CH}_2\text{ --NH-- (CH}_2\text{) }_2\text{ --}$
 $\text{--CH}_2\text{ --NH-- (CH}_2\text{) }_3\text{ --}$
 $\text{--CH}_2\text{ --NH-- (CH}_2\text{) }_4\text{ --}$
 $\text{--CH}_2\text{ --NH-- (CH}_2\text{) }_5\text{ --}$
 $\text{--CH}_2\text{ --S-- (CH}_2\text{) }_2\text{ --}$
 $\text{--CH}_2\text{ --S-- (CH}_2\text{) }_3\text{ --}$
 $\text{--CH}_2\text{ --S-- (CH}_2\text{) }_4\text{ --}$
 $\text{--CH}_2\text{ --S-- (CH}_2\text{) }_5\text{ --}$
 $\text{--CH}_2\text{ --S (O) -- (CH}_2\text{) }_2\text{ --}$

TABLE 1 (contn'd)

$-\text{CH}_2 - \text{S} (\text{O}) - (\text{CH}_2)_3 -$
 $-\text{CH}_2 - \text{S} (\text{O}) - (\text{CH}_2)_4 -$
 $-\text{CH}_2 - \text{S} (\text{O}) - (\text{CH}_2)_5 -$
 $-\text{CH}_2 - \text{S} (\text{O})_2 - (\text{CH}_2)_2 -$
 $-\text{CH}_2 - \text{S} (\text{O})_2 - (\text{CH}_2)_3 -$
 $-\text{CH}_2 - \text{S} (\text{O})_2 - (\text{CH}_2)_4 -$
 $-\text{CH}_2 - \text{S} (\text{O})_2 - (\text{CH}_2)_5 -$
 $-\text{CH}_2 - \text{O} - \text{C} (= \text{O}) - (\text{CH}_2)_2 -$
 $-\text{CH}_2 - \text{O} - \text{C} (= \text{O}) - (\text{CH}_2)_3 -$
 $-\text{CH}_2 - \text{O} - \text{C} (= \text{O}) - (\text{CH}_2)_4 -$
 $-\text{CH}_2 - \text{O} - \text{C} (= \text{O}) - (\text{CH}_2)_5 -$
 $-\text{CH}_2 - \text{NH} - \text{C} (= \text{O}) - (\text{CH}_2)_2 -$
 $-\text{CH}_2 - \text{NH} - \text{C} (= \text{O}) - (\text{CH}_2)_3 -$
 $-\text{CH}_2 - \text{NH} - \text{C} (= \text{O}) - (\text{CH}_2)_4 -$
 $-\text{CH}_2 - \text{NH} - \text{C} (= \text{O}) - (\text{CH}_2)_5 -$
 $-\text{CH}_2 - \text{C} (= \text{O}) - \text{O} - (\text{CH}_2)_2 -$
 $-\text{CH}_2 - \text{C} (= \text{O}) - \text{O} - (\text{CH}_2)_3 -$
 $-\text{CH}_2 - \text{C} (= \text{O}) - \text{O} - (\text{CH}_2)_4 -$
 $-\text{CH}_2 - \text{C} (= \text{O}) - \text{O} - (\text{CH}_2)_5 -$
 $-\text{CH}_2 - \text{C} (= \text{O}) - \text{NH} - (\text{CH}_2)_2 -$
 $-\text{CH}_2 - \text{C} (= \text{O}) - \text{NH} - (\text{CH}_2)_3 -$
 $-\text{CH}_2 - \text{C} (= \text{O}) - \text{NH} - (\text{CH}_2)_4 -$
 $-\text{CH}_2 - \text{C} (= \text{O}) - \text{NH} - (\text{CH}_2)_5 -$

TABLE 2



(wherein R^8 and R^9 in Table 2 are as defined in Table 3.)

TABLE 3

R ⁸	R ⁹
CH ₃	CH ₃
CH ₂ CH ₃	CH ₂ CH ₃
(CH ₂) ₂ CH ₃	(CH ₂) ₂ CH ₃
CH (CH ₃) ₂	CH (CH ₃) ₂
(CH ₂) ₃ CH ₃	(CH ₂) ₃ CH ₃
CH ₂ CH (CH ₃) ₂	CH ₂ CH (CH ₃) ₂
CH (CH ₃) CH ₂ CH ₃	CH (CH ₃) CH ₂ CH ₃
(CH ₂) ₄ CH ₃	(CH ₂) ₄ CH ₃
(CH ₂) ₅ CH ₃	(CH ₂) ₅ CH ₃
CH ₂ CH=CH ₂	CH ₂ CH=CH ₂
CH ₂ CH=CHCH ₃	CH ₂ CH=CHCH ₃
CH ₂ CH=C (CH ₃) ₂	CH ₂ CH=C (CH ₃) ₂
CH ₂ CH=CHC l	CH ₂ CH=CHC l
CH ₂ CH=CC l CH ₃	CH ₂ CH=CC l CH ₃
CH ₂ CH=CC l ₂	CH ₂ CH=CC l ₂
CH ₂ CH=CB r ₂	CH ₂ CH=CB r ₂
CH ₂ CH=CC l CF ₃	CH ₂ CH=CC l CF ₃
CH ₂ C≡CH	CH ₂ C≡CH
CH ₂ C≡CC l	CH ₂ C≡CC l
CH ₂ C≡CCH ₃	CH ₂ C≡CCH ₃
cyclohexyl	cyclohexyl
(CH ₂) ₂ OCH ₃	(CH ₂) ₂ OCH ₃

TABLE 3 (cont'd)

R ⁸	R ⁹
CH ₃	H
CH ₂ CH ₃	H
(CH ₂) ₂ CH ₃	H
CH (CH ₃) ₂	H
(CH ₂) ₃ CH ₃	H
CH ₂ CH (CH ₃) ₂	H
CH (CH ₃) CH ₂ CH ₃	H
C (CH ₃) ₃	H
(CH ₂) ₄ CH ₃	H
(CH ₂) ₂ CH (CH ₃) ₂	H
CH ₂ CH (CH ₃) CH ₂ CH ₃	H
CH ₂ C (CH ₃) ₃	H
CH (CH ₃) (CH ₂) ₂ CH ₃	H
CH (CH ₃) CH (CH ₃) ₂	H
C (CH ₃) ₂ CH ₂ CH ₃	H
CH (CH ₂ CH ₃) ₂	H
(CH ₂) ₅ CH ₃	H
CH (CH ₃) CH ₂ CH (CH ₃) ₂	H
(CH ₂) ₂ C (CH ₃) ₃	H
CH ₂ CH=CH ₂	H
CH ₂ CH=CHCH ₃	H
CH ₂ CH=C (CH ₃) ₂	H
CH ₂ CH=CHCl	H
CH ₂ CH=CClCH ₃	H

TABLE 3 (cont'd)

R^8	R^9
$CH_2 CH=CCl_2$	H
$CH_2 CH=CB r_2$	H
$CH_2 CH=CClCF_3$	H
$CH_2 C \equiv CH$	H
$CH_2 C \equiv CCH_3$	H
$CH_2 C \equiv CC l$	H
cyclopropyl	H
cyclobutyl	H
cyclopentyl	H
cyclohexyl	H
2-methylcyclohexyl	H
3-methylcyclohexyl	H
4-methylcyclohexyl	H
$(CH_2)_2 OCH_3$	H
$(CH_2)_3 OCH_3$	H
$CH (CH_3) (CH_2) OCH_3$	H
cyclopropylmethyl	H
cyclohexylmethyl	H
1-cyclohexylethyl	H
$CH_2 CH_3$	CH_3
$(CH_2)_2 CH_3$	CH_3
$CH (CH_3)_2$	CH_3
$(CH_2)_3 CH_3$	CH_3
$(CH_2)_4 CH_3$	CH_3

TABLE 3 (cont'd)

R ⁸	R ⁹
(CH ₂) ₅ CH ₃	CH ₃
CH ₂ CH=CH ₂	CH ₃
(CH ₂) ₅ CH ₃	CH ₂ CH ₃
CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃
cyclohexyl	CH ₂ CH ₃
cyclopropylmethyl	(CH ₂) ₂ CH ₃

TABLE 3 (cont'd)

$-R^8 - R^9 -$
$-(CH_2)_2 -$
$-CH_2 CH(CH_3) -$
$-(CH_2)_3 -$
$-(CH_2)_4 -$
$-CH(CH_3)(CH_2)_2 CH(CH_3) -$
$-CH_2 CH=CHCH_2 -$
$-CH(CH_3) CH=CHCH_2(CH_3) -$
$-(CH_2)_5 -$
$-(CH_2)_4 CH(CH_3) -$
$-(CH_2)_4 CH(CH_2CH_3) -$
$-(CH_2)_3 CH(CH_3) CH_2 -$
$-(CH_2)_2 CH(CH_3)(CH_2)_2 -$
$-(CH_2)_3 C(CH_3)_2 CH_2 -$
$-CH(CH_3)(CH_2)_3 CH(CH_3) -$
$-CH_2 CH(CH_3) CH_2 CH(CH_3) CH_2 -$
$-C(CH_3)_2(CH_2)_3 C(CH_3)_2 -$
$-(CH_2)_2 CH=CHCH_2 -$
$-(CH_2)_6 -$
$-(CH_2) CH(CH_3) CH_2 C(CH_3)_2 CH_2 -$

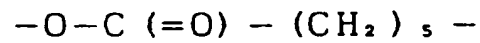
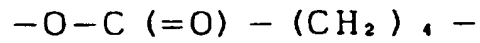
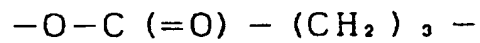
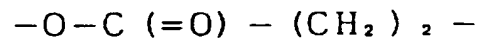
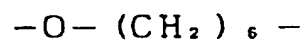
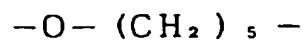
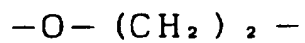
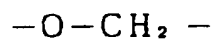
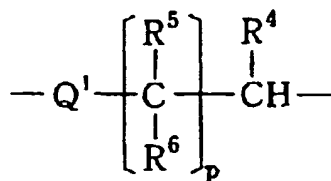
TABLE 4

TABLE 5

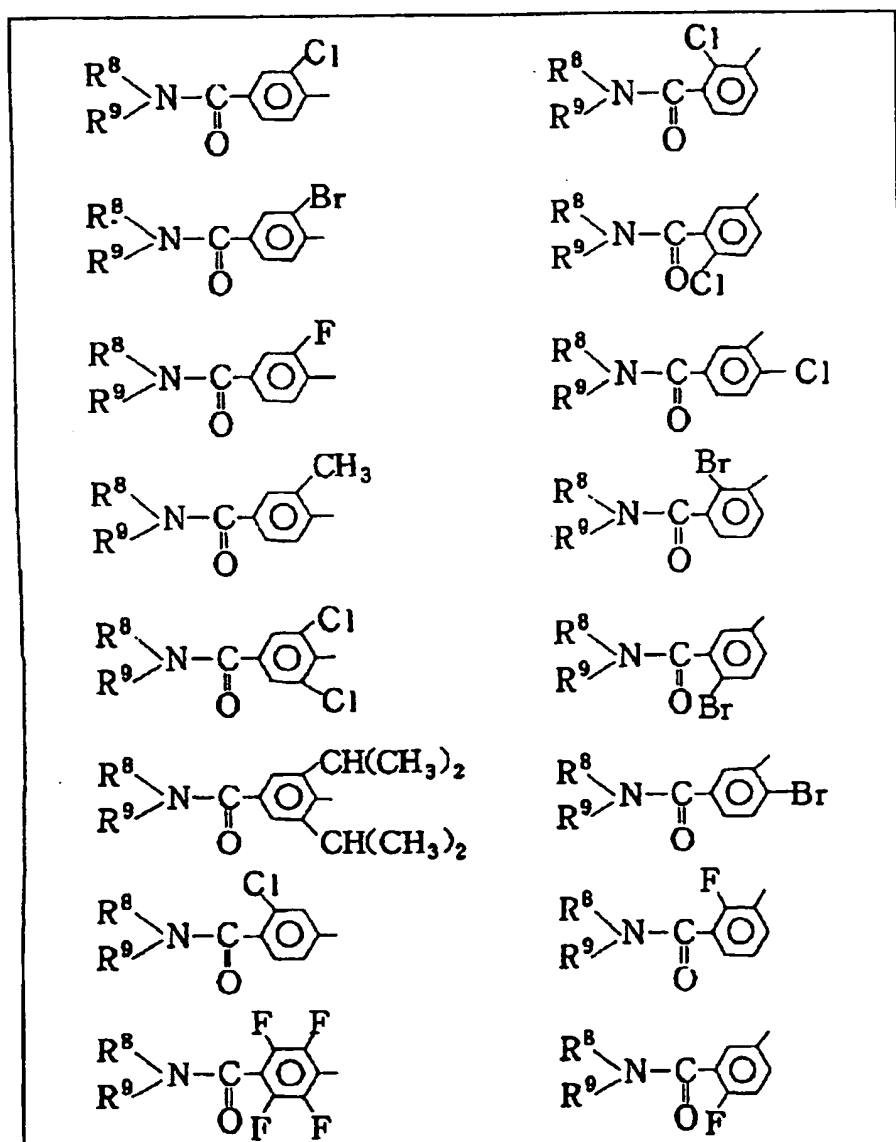
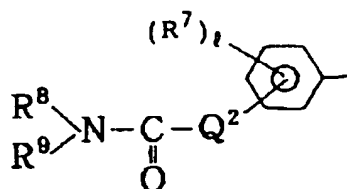


TABLE 5 (cont'd)

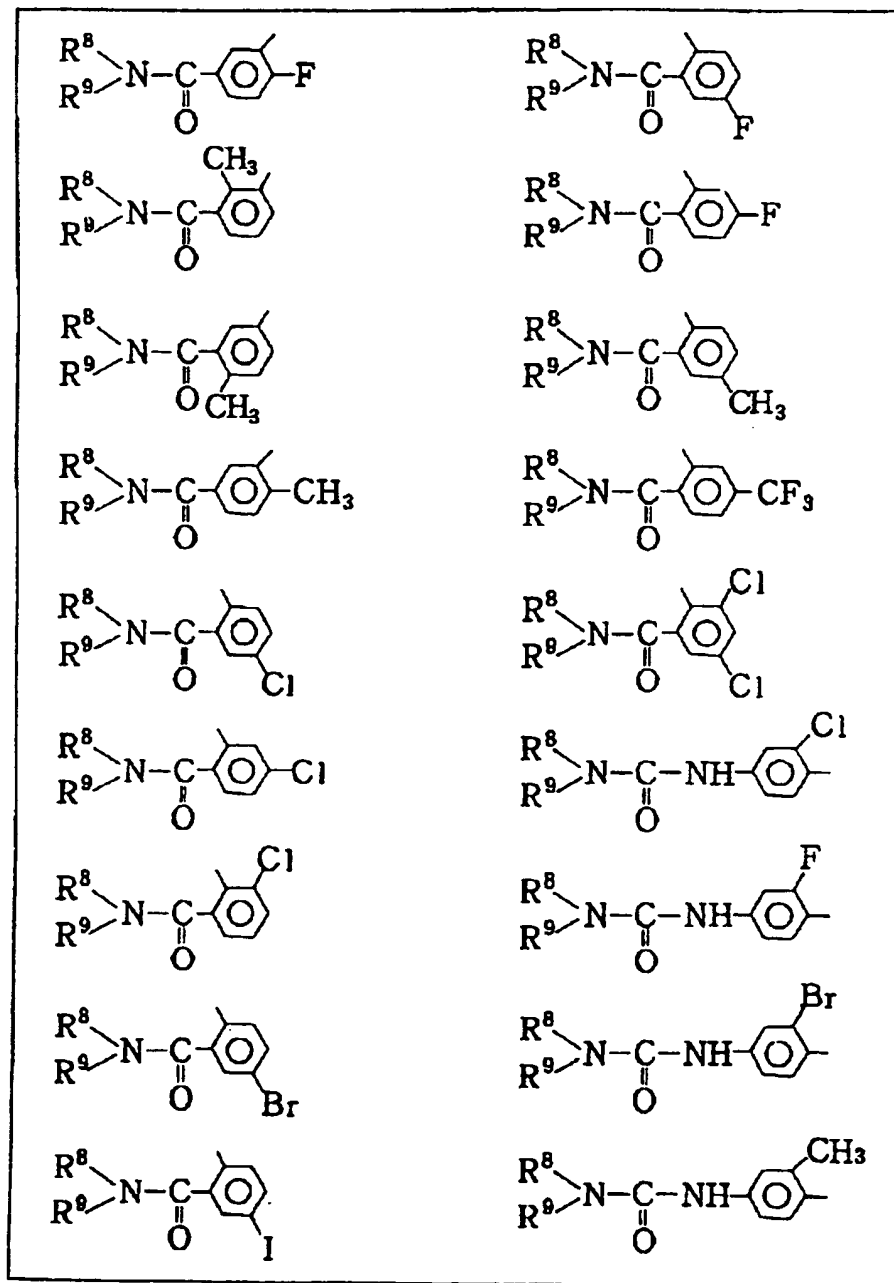


TABLE 5 (cont'd)

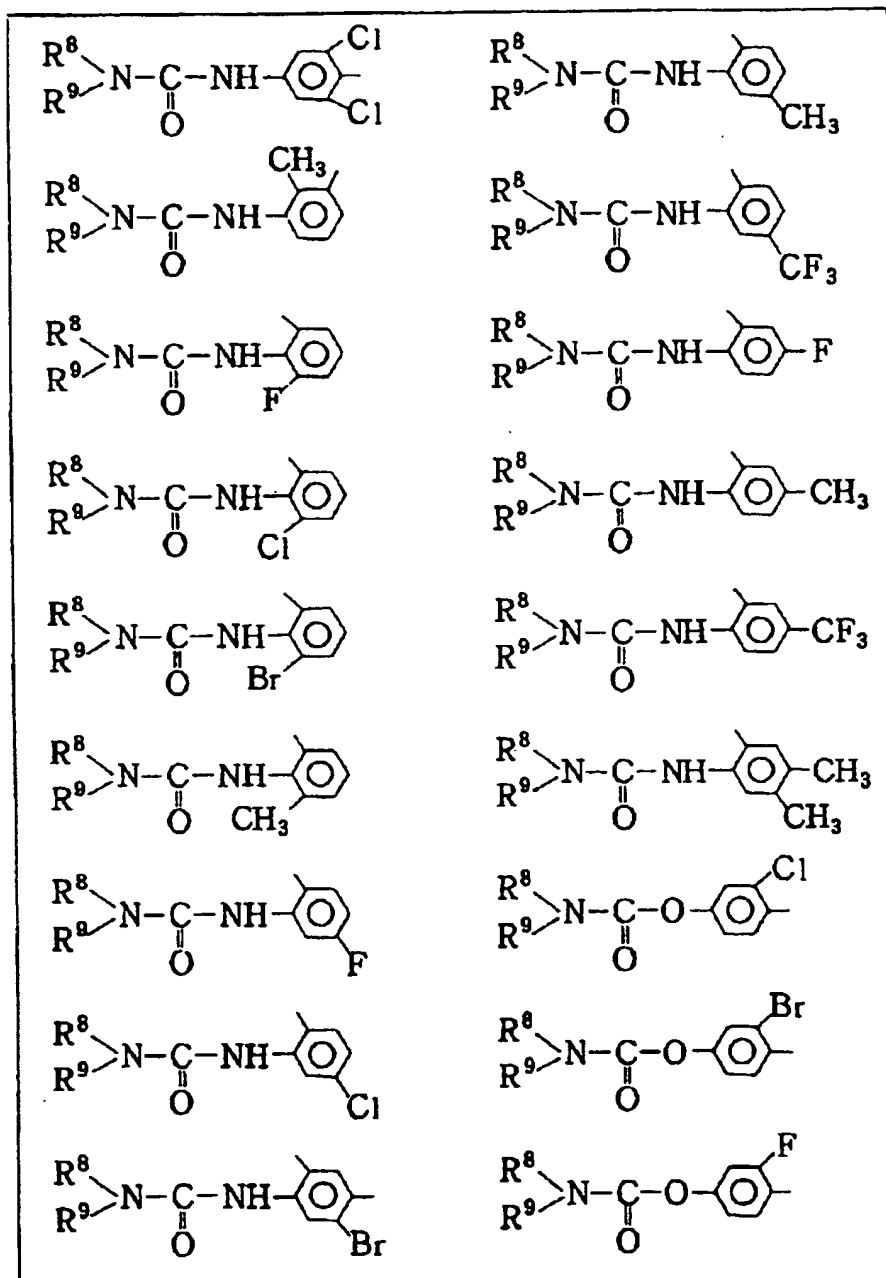


TABLE 5 (cont'd)

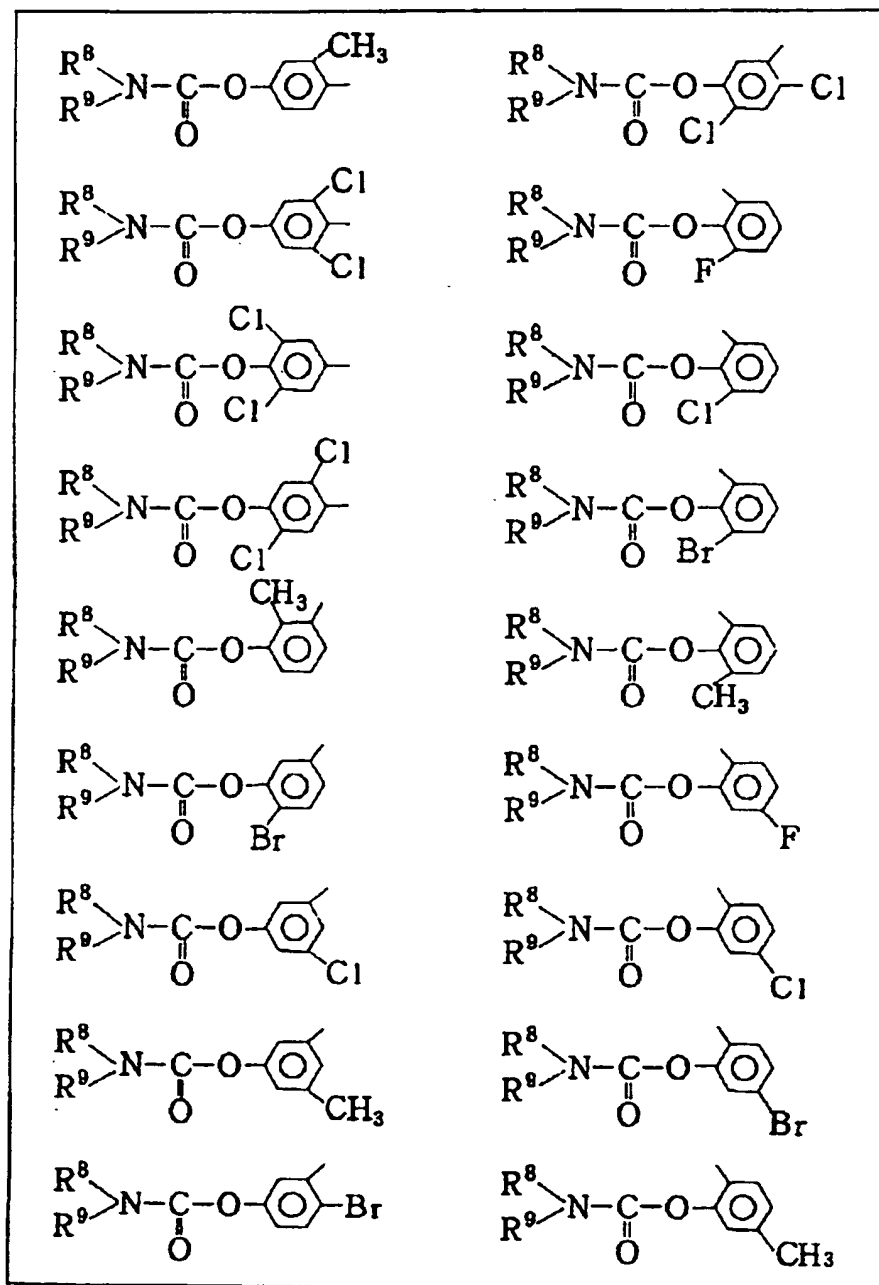
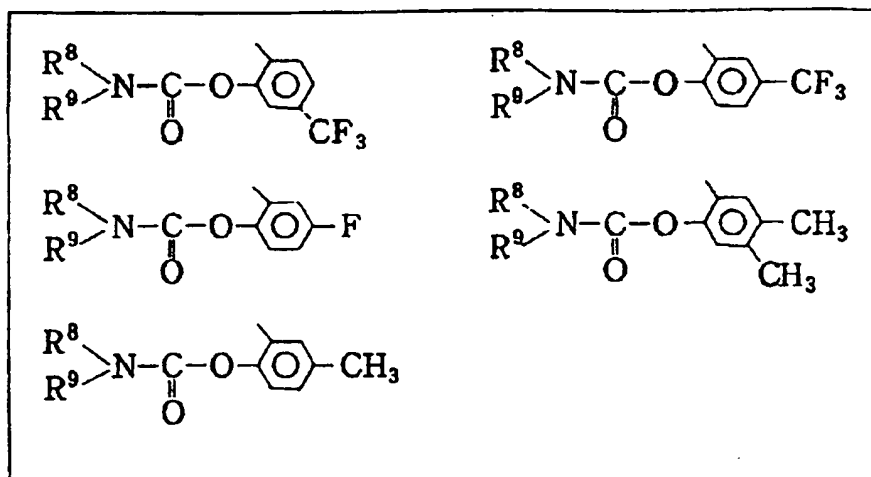


TABLE 5 (cont'd)

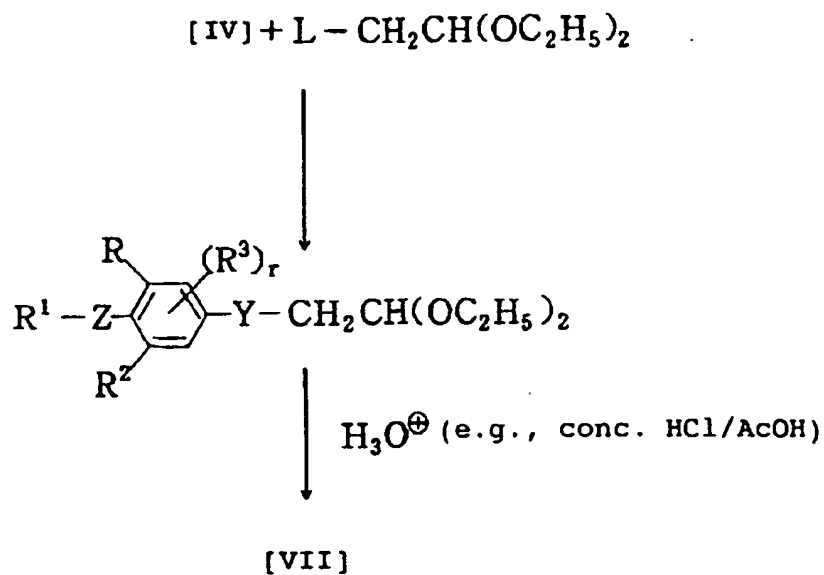
(wherein R^8 and R^9 in Table 5 are as defined in Table 6.)

TABLE 6

R ⁸	R ⁹
(CH ₂) ₂ CH ₃	(CH ₂) ₂ CH ₃
(CH ₂) ₃ CH ₃	(CH ₂) ₃ CH ₃
CH(CH ₃) ₂	CH(CH ₃) ₂
CH ₂ CH=CH ₂	CH ₂ CH=CH ₂
CH ₂ C≡CH	CH ₂ C≡CH
(CH ₂) ₂ CH ₃	H
(CH ₂) ₃ CH ₃	H
CH ₂ CH=CH	H
CH ₂ C≡CH	H
CH(CH ₃) ₂	H
—(CH ₂) ₄ —	
—CH ₂ CH=CHCH ₂ —	
—(CH ₂) ₅ —	

The aldehyde compounds of the general formula [VII], which are intermediates for the production of the present compounds, can be produced, for example, according to the following scheme 1:

SCHEME 1

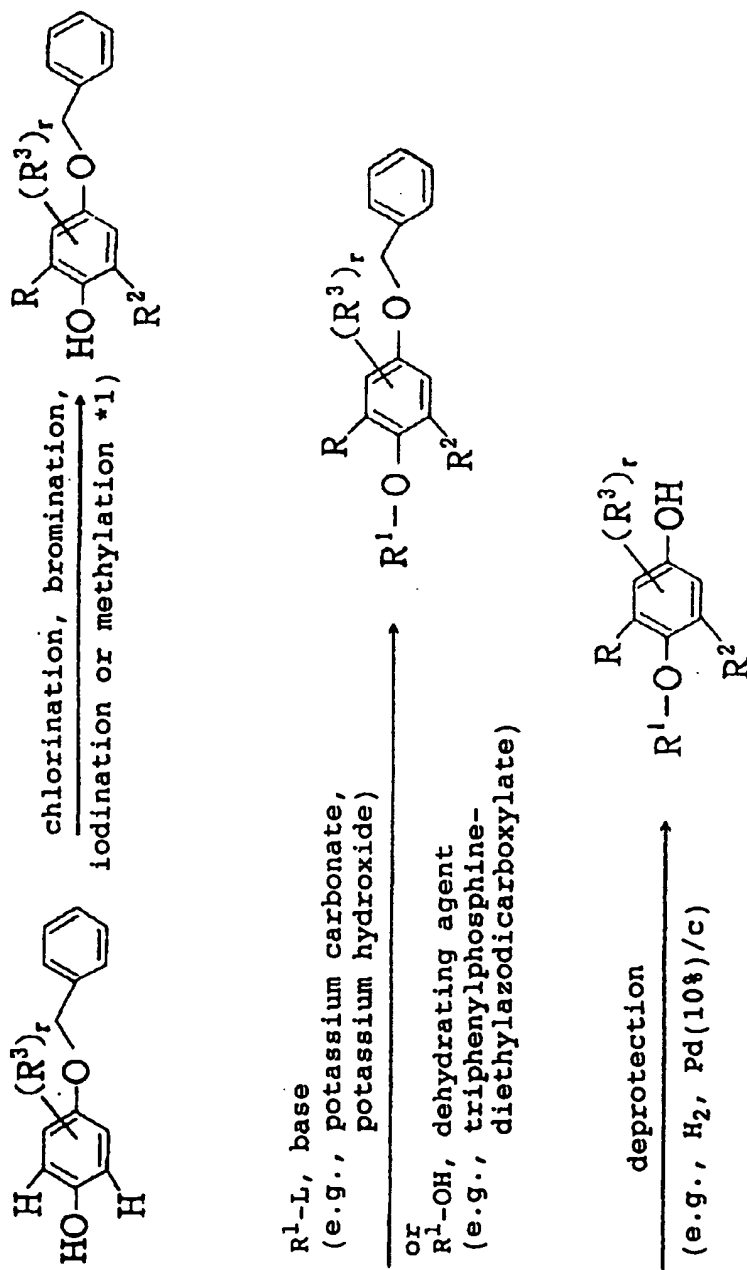


wherein all the symbols are as defined above.

- 5 The compounds of the general formula [IV], which are intermediates for the production of the present compounds, can be produced, for example, according to the following schemes 2 to 6:

SCHEME 2

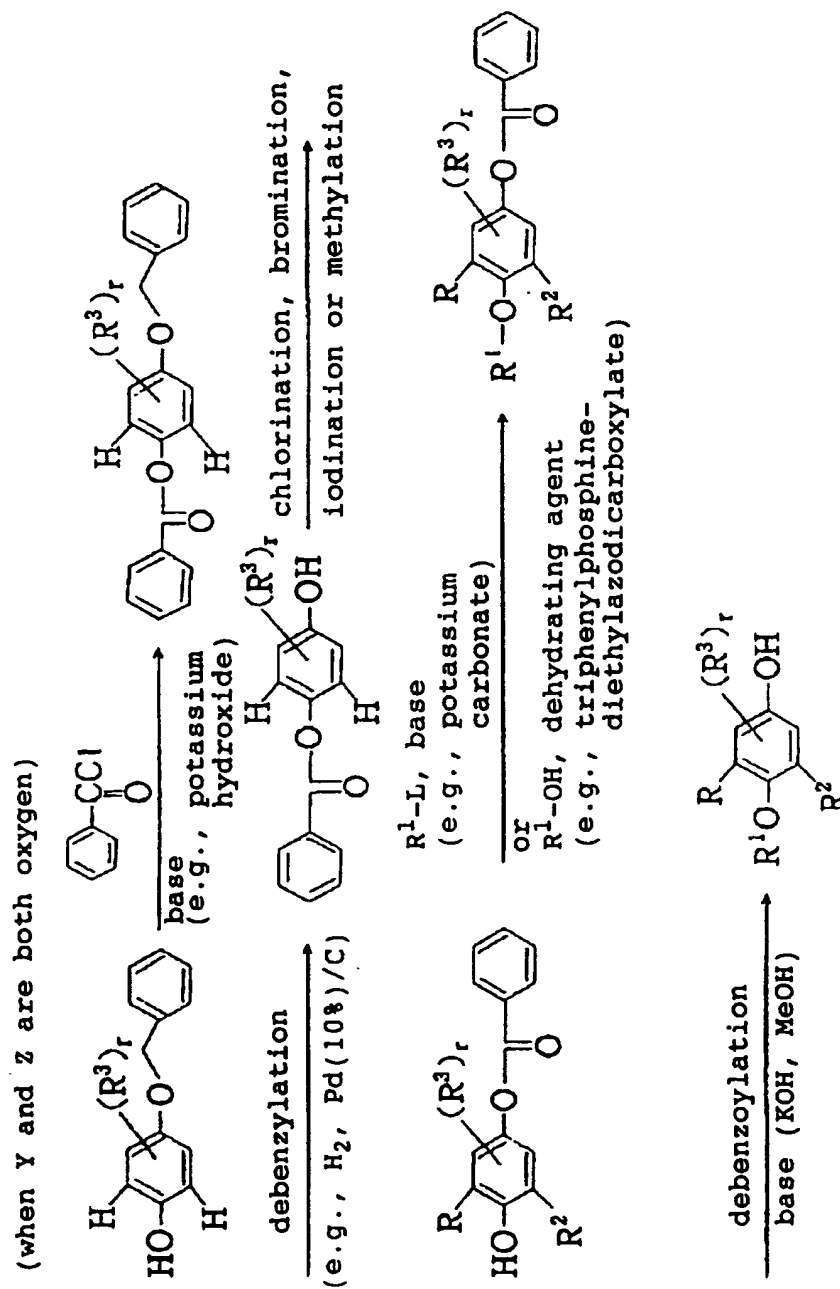
(when Y and Z are both oxygen)



*1): e.g., Tetrahedron Lett., 889 (1974).

wherein R, R¹, R², R³, r and L are as defined above.

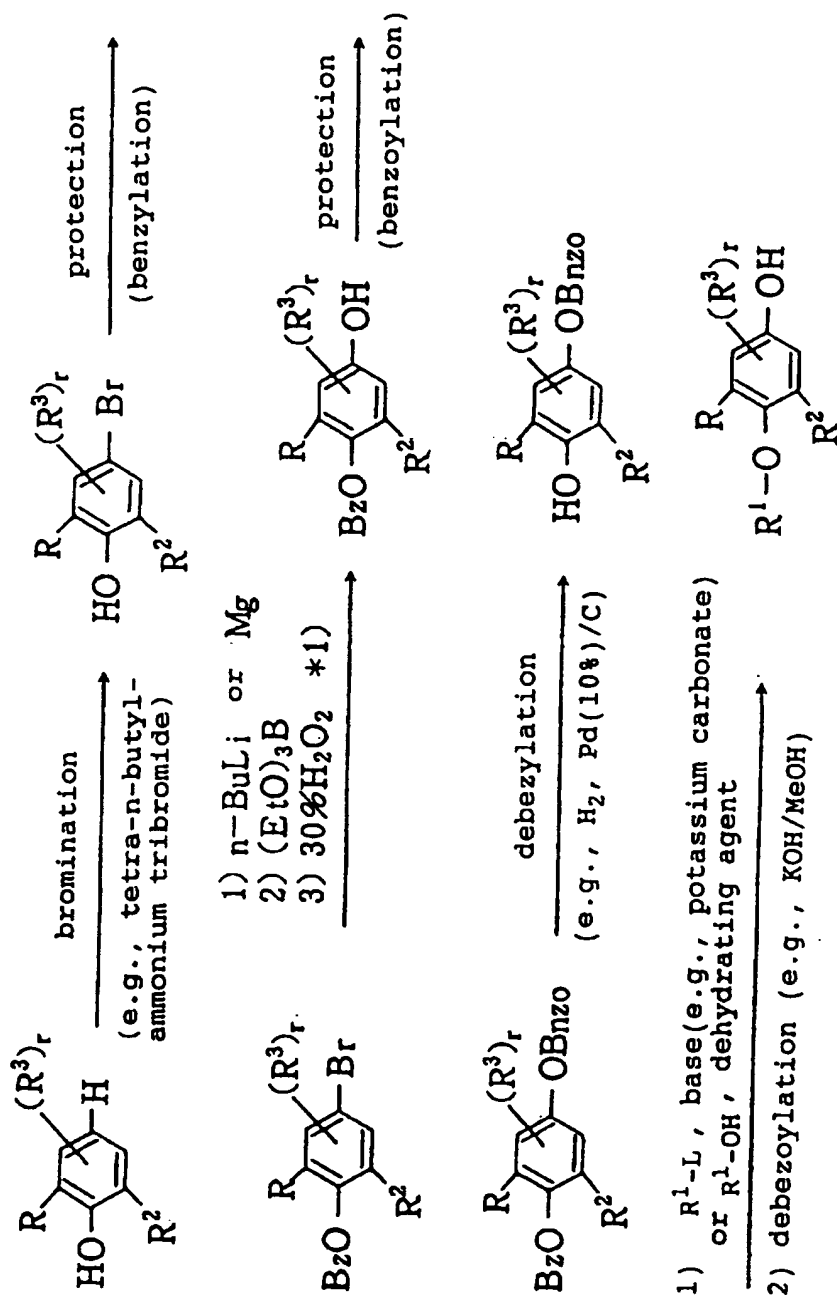
SCHEME 3



wherein R , R^1 , R^2 , R^3 , r and L are as defined above.

SCHEME 3 (contn'd)

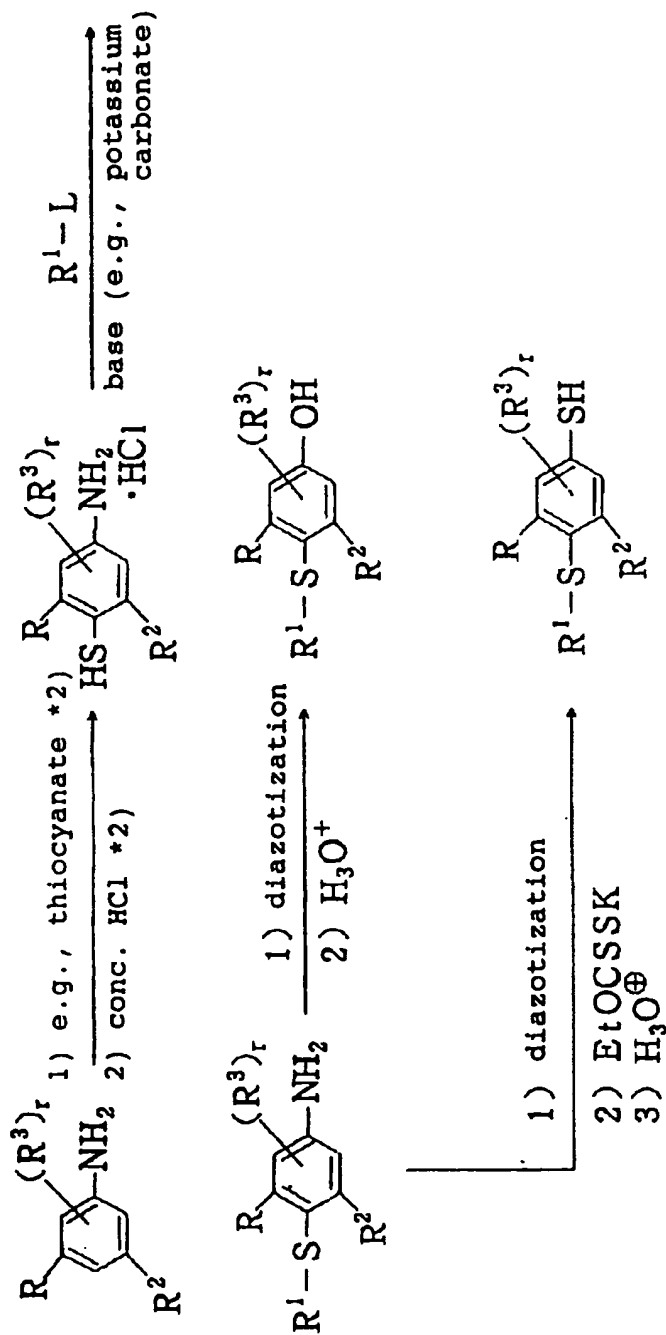
(Y and Z are both oxygen)

*1): J. Org. Chem., 22, 1001(1957)

wherein Bz is benzoyl, Bnzo is benzoyl, and the other symbols are as defined above.

SCHEME 4

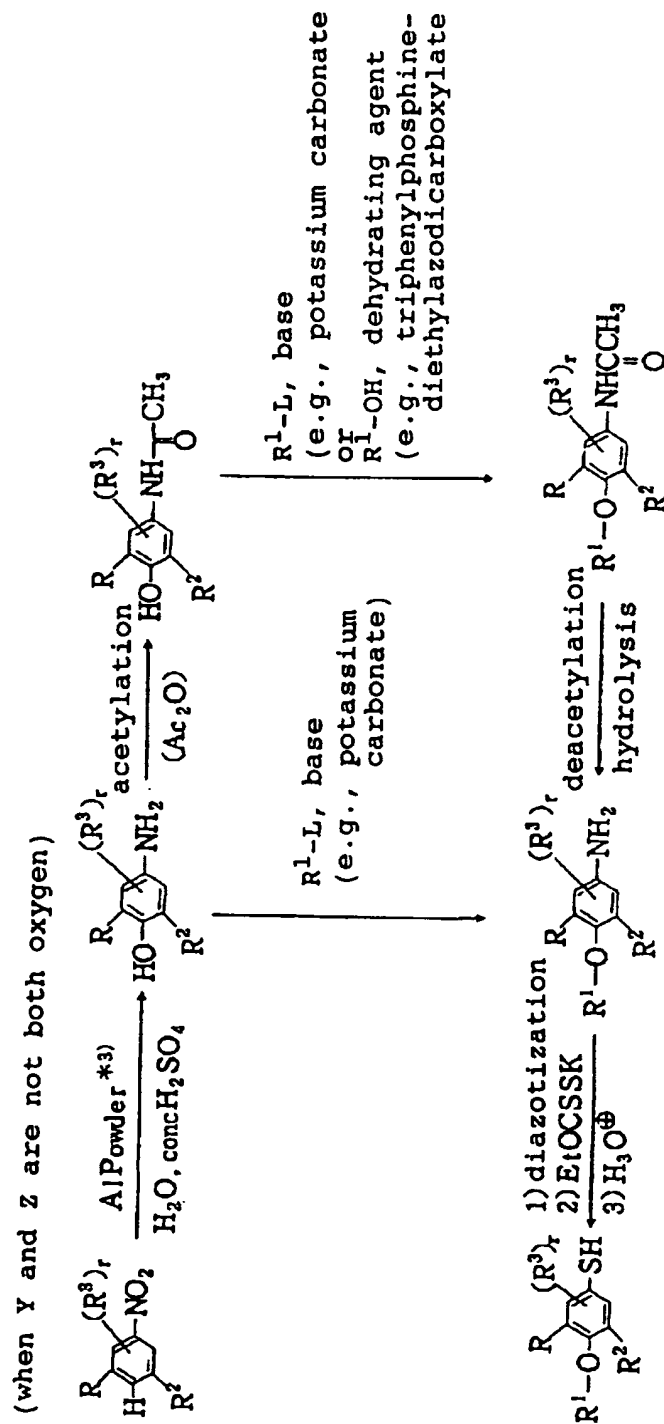
(when Y and Z are not both oxygen)



2): JP 60-181067 A

wherein R , R^1 , R^2 , R^3 , r and L are as defined above.

SCHEME 5

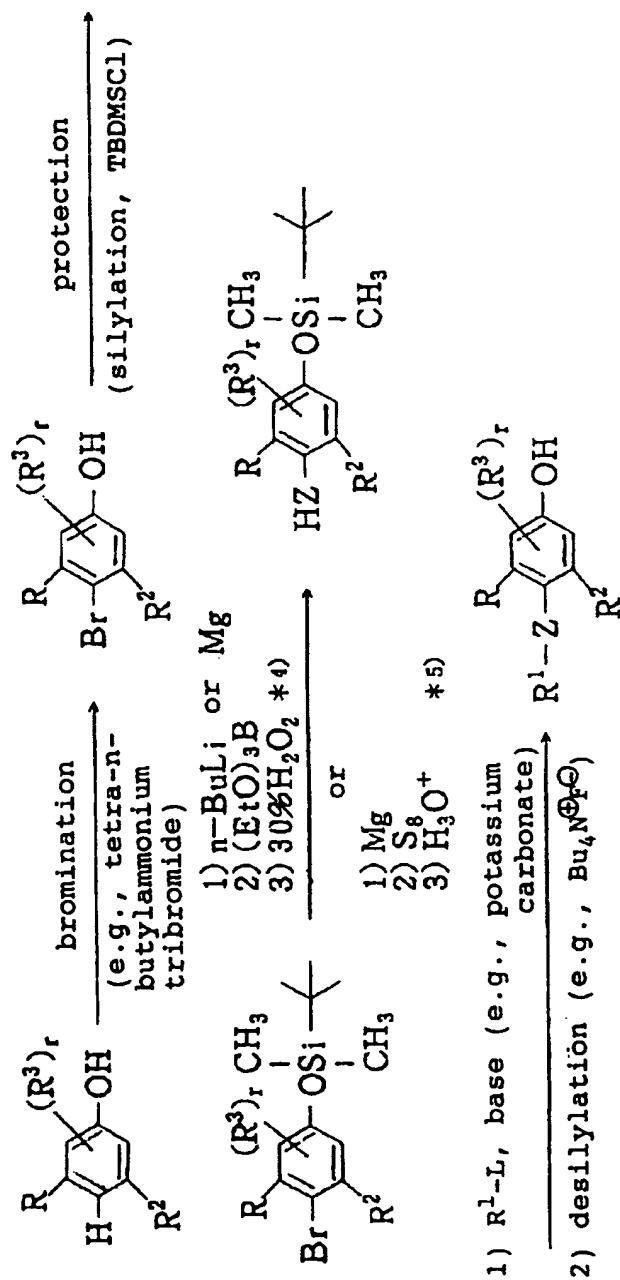


*3): H. J. Shine, "Aromatic Rearrangement", Elsevier, 182 (1967)

wherein R, R¹, R², R³, r and L are as defined above.

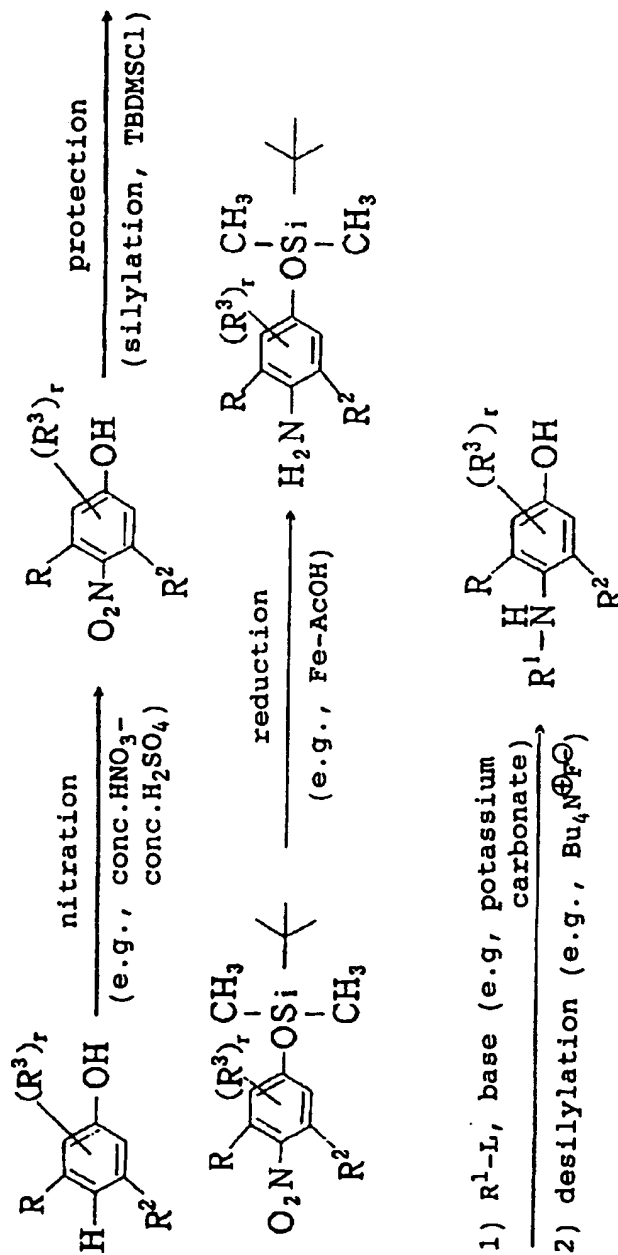
SCHEME 6

(when Y is oxygen)

*4): J. Org. Chem., 22, 1001 (1957)*5): Ber., 72, 594 (1939)wherein R , R^1 , R^2 , R^3 , r , L and Z are as defined above.

SCHEME 6 (contn'd)

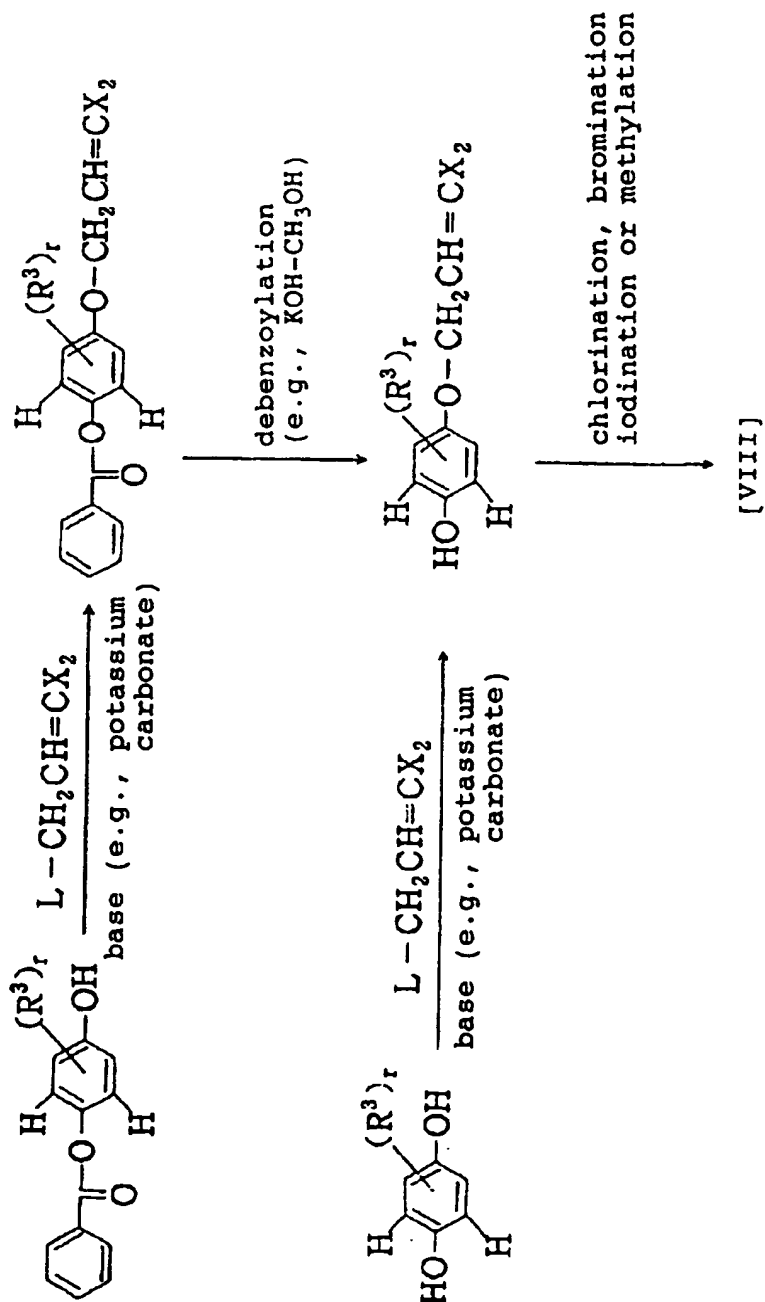
(when Y is oxygen)



wherein R, R¹, R², R³, r and L are as defined above.

The compounds of the general formula [VIII], which are intermediates for the production of the present compounds, can be produced, for example, according to the following scheme 7:

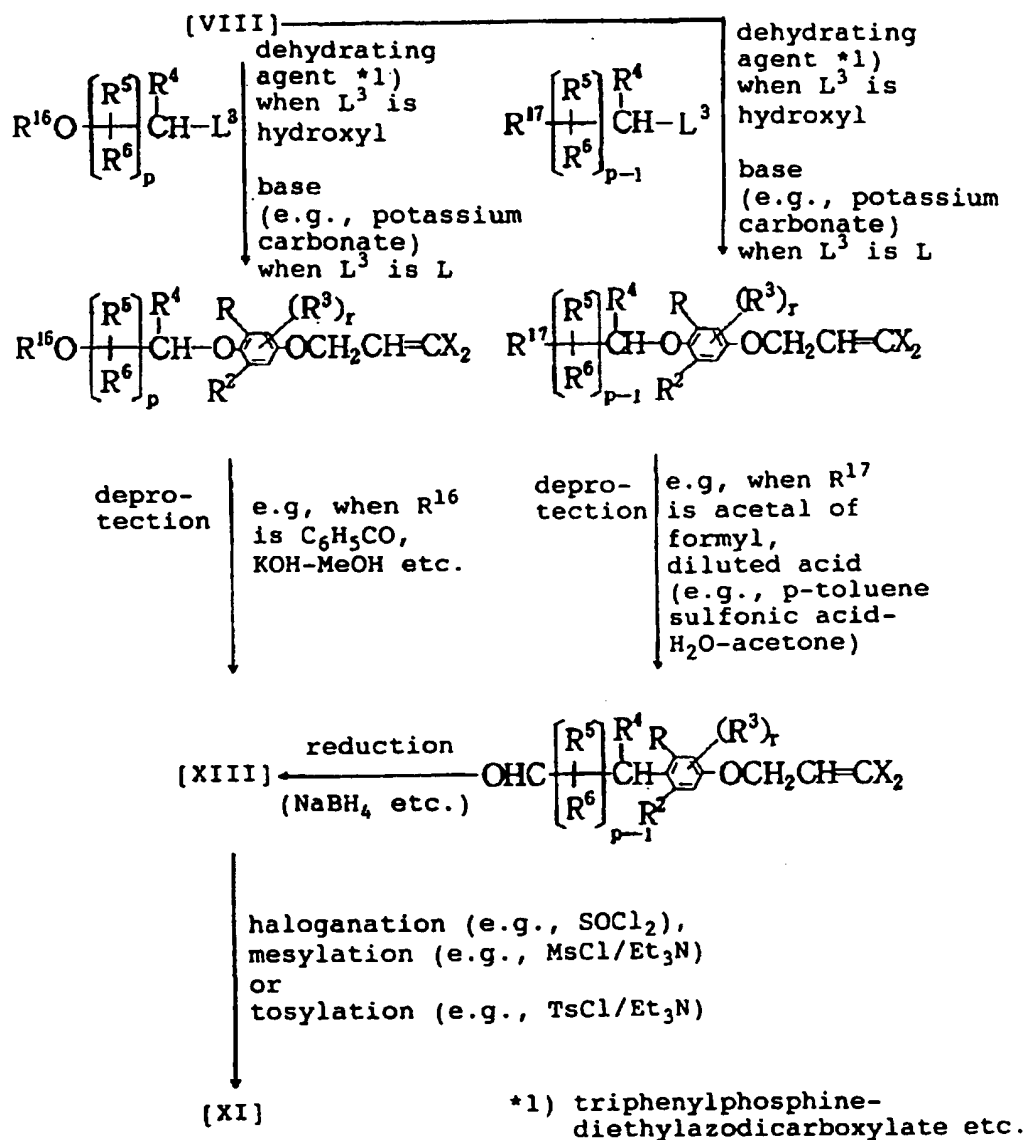
SCHEME 7



wherein R^3 , r , X and L are as defined above.

The compounds of the general formula [XI] or [XIII] wherein Y and Z are both oxygen, which are intermediates for the production of the present compounds, can be produced, for example, according to the following scheme 8 or 9:

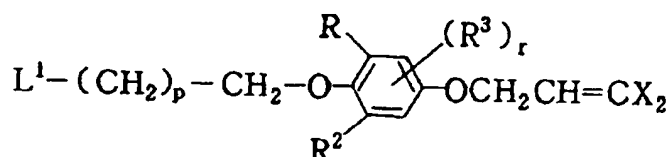
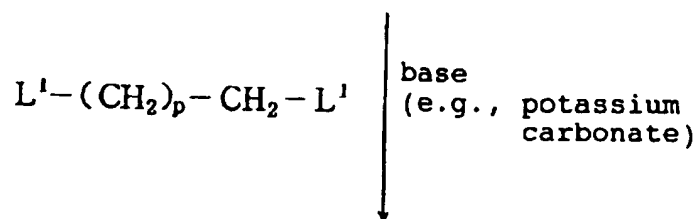
SCHEME 8



wherein R¹⁶ is a protecting group (e.g., benzoyl) for alcohols, R¹⁷ is an equivalent of
5 formyl (e.g., an acetal of formyl), Ms is mesyl, Ts is tosyl, and the other symbols are as defined above.

SCHEME 9

[VIII]

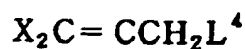
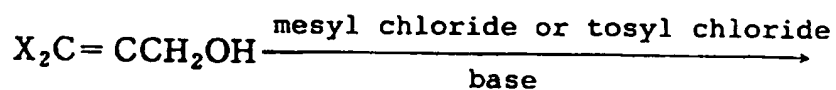
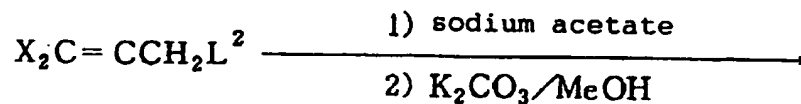
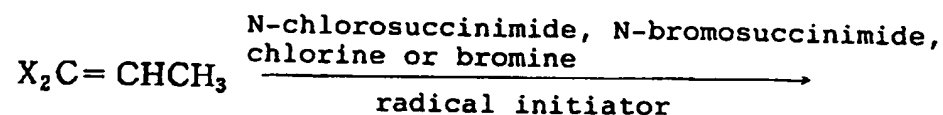


[XI] (wherein R^4 , R^5 and R^6 are hydrogen, and Y and Z are oxygen)

wherein all the symbols are as defined above.

The halide compounds of the general formula [V] and the alcohol compounds of the general formula [VI], which are intermediates for the production of the present compounds, can be obtained from commercial sources or can be produced according to the following scheme 10:

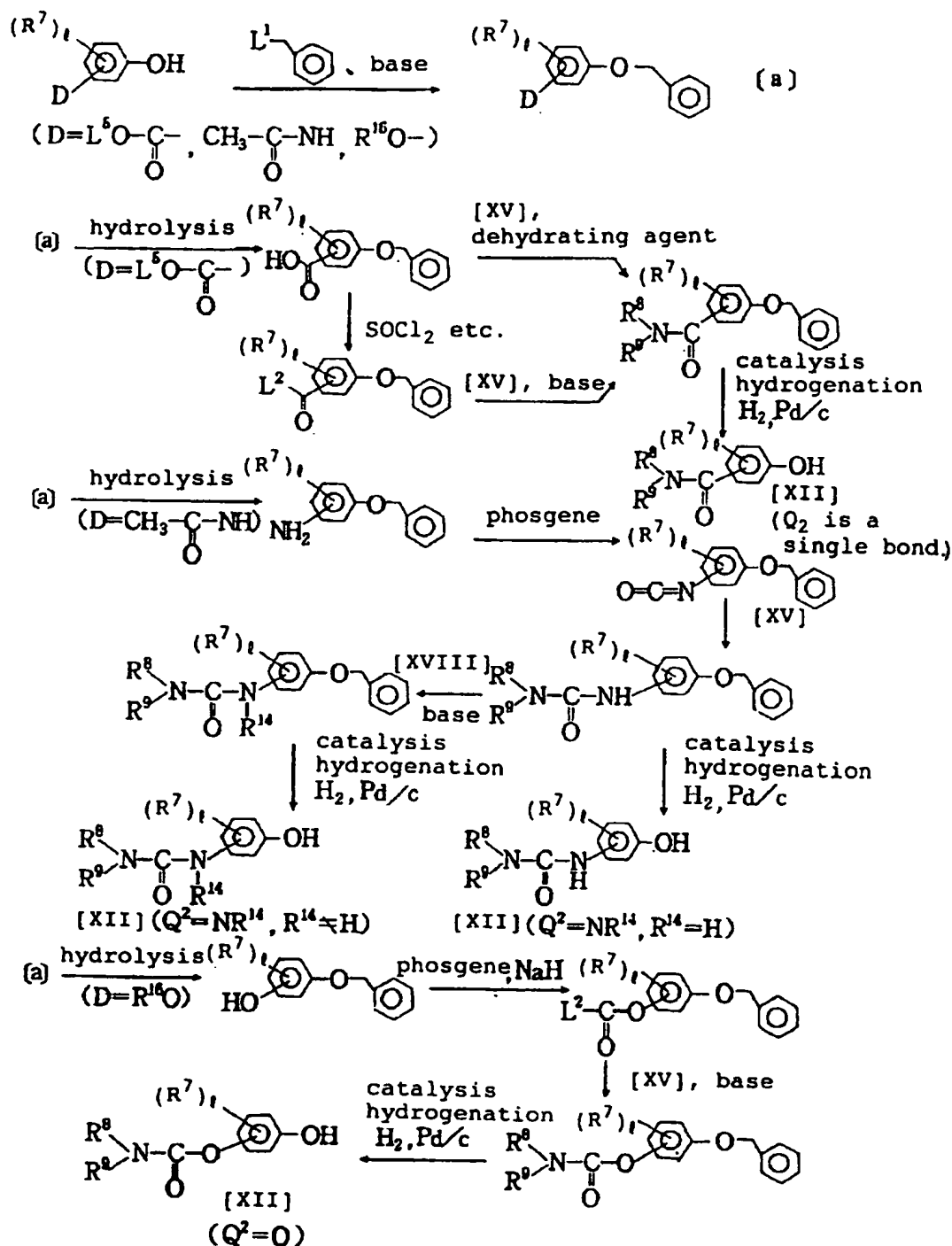
SCHEME 10



wherein L^4 is mesyloxy or tosyloxy, and L^2 and X are as defined above.

The compounds of the general formula [XII], which are intermediates for the production of the present compounds, can be produced, for example, according to the following scheme 11:

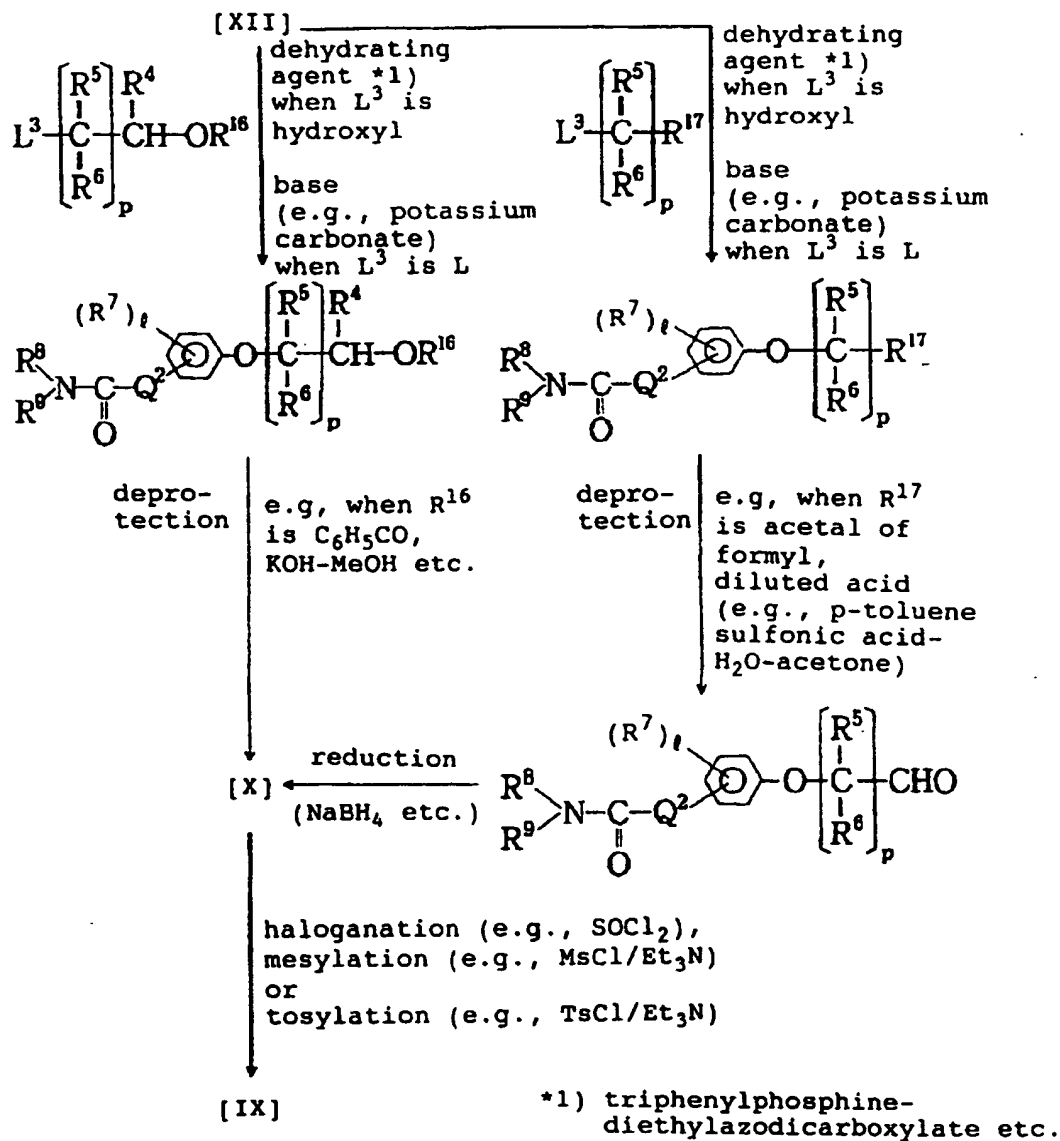
SCHEME 11



wherein L⁵ is methyl, ethyl or propyl, and R¹⁶ is as defined above.

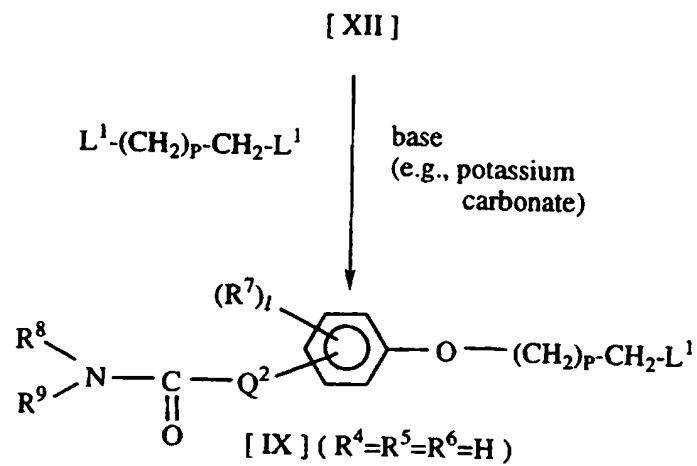
The compounds of the general formula [IX] or [X], which are intermediates for the production of the present compounds, can be produced, for example, according to the following scheme 12:

SCHEME 12



wherein all the symbols are as defined above.

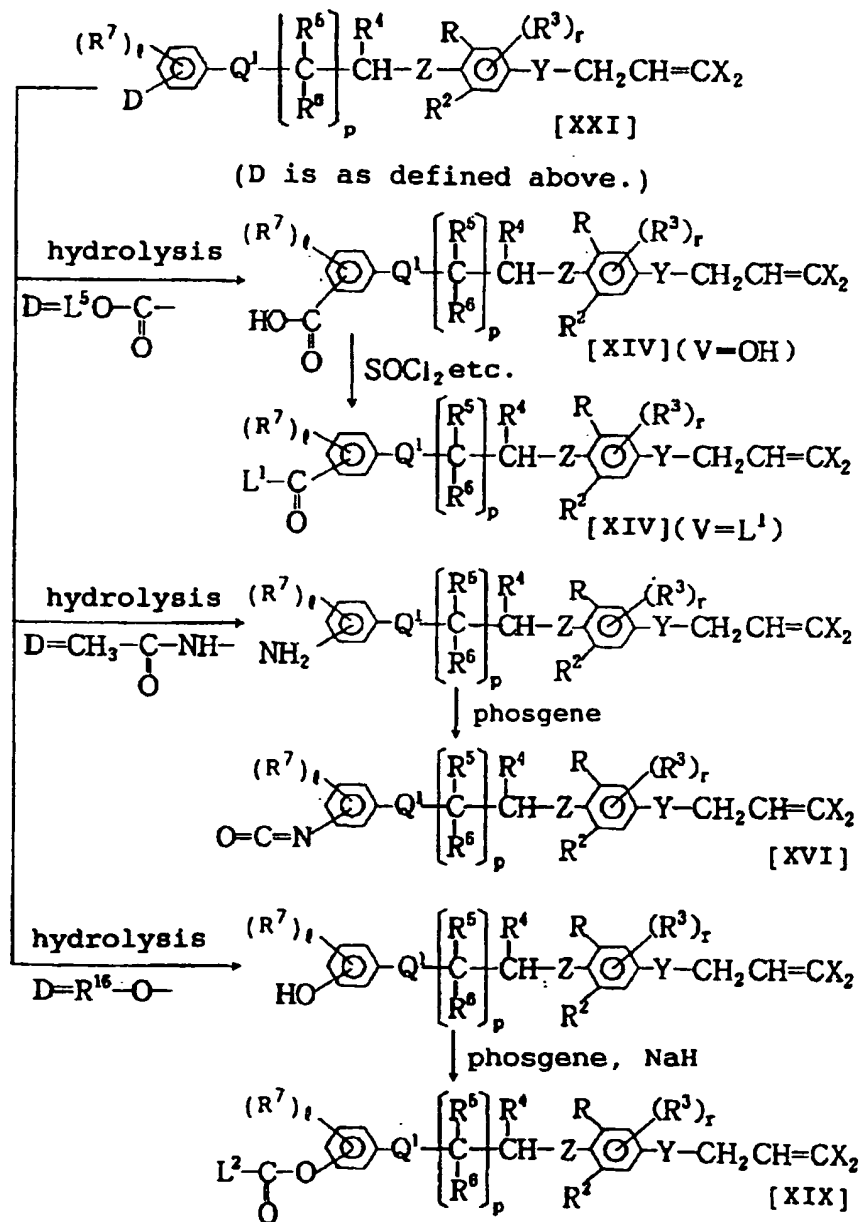
SCHEME 12 (contn'd)



wherein all the symbols are as defined above.

The compounds of the general formula [XIV], [XV] or [XIX], which are intermediates for the production of the present compounds, can be produced, for example, according to the following scheme 13:

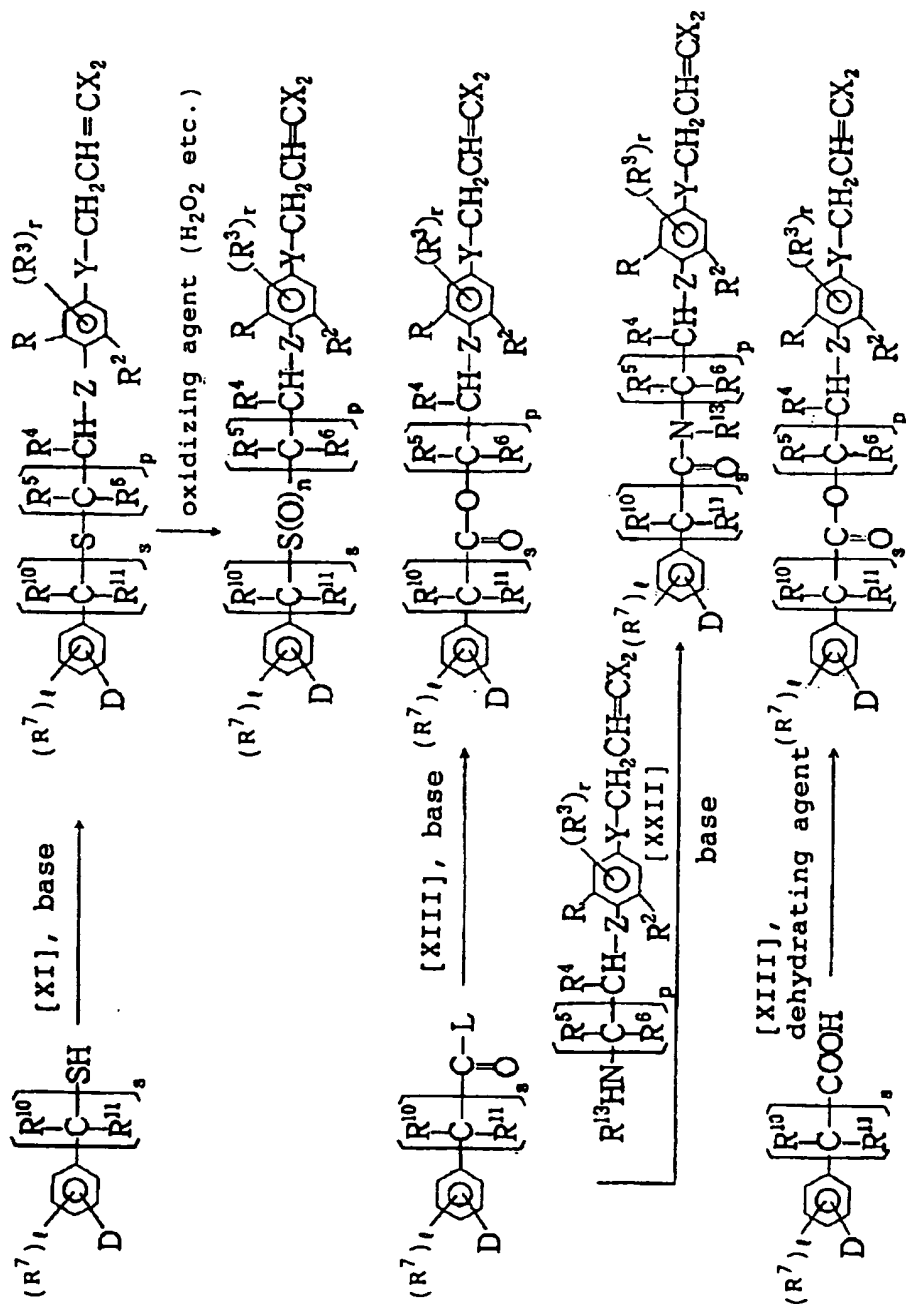
SCHEME 13



wherein all the symbols are as defined above.

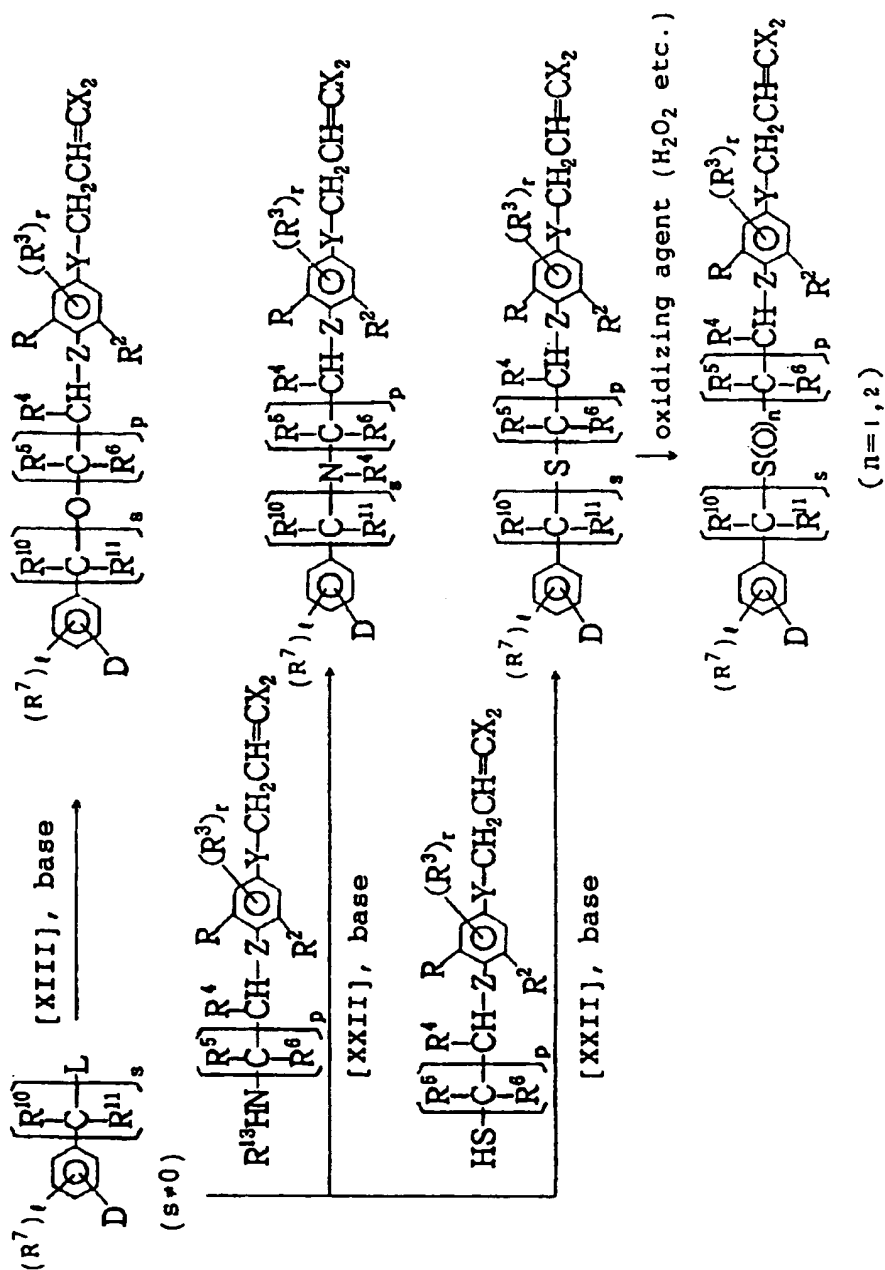
The compounds of the general formula [XXI], which are used in the scheme 13, can be produced, for example, according to the following schemes 14 to 16:

SCHEME 15



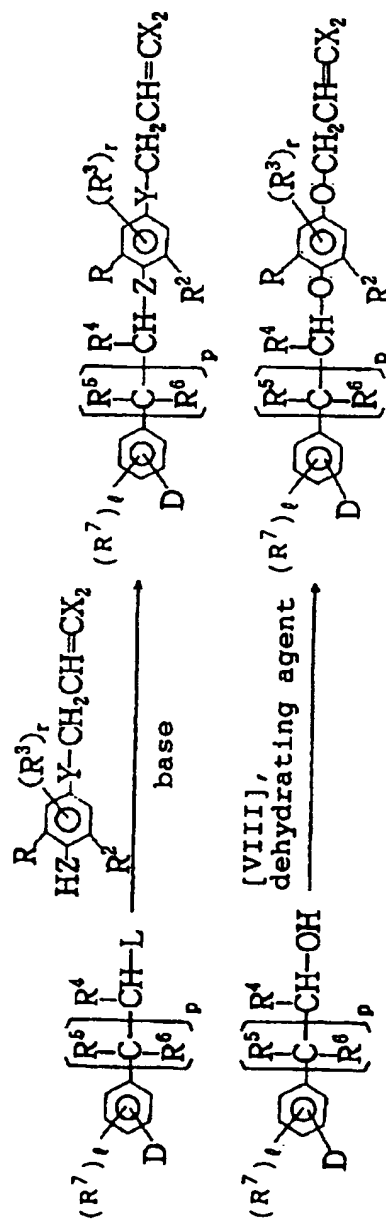
wherein all the symbols are as defined above.

SCHEME 16



wherein all the symbols are as defined above.

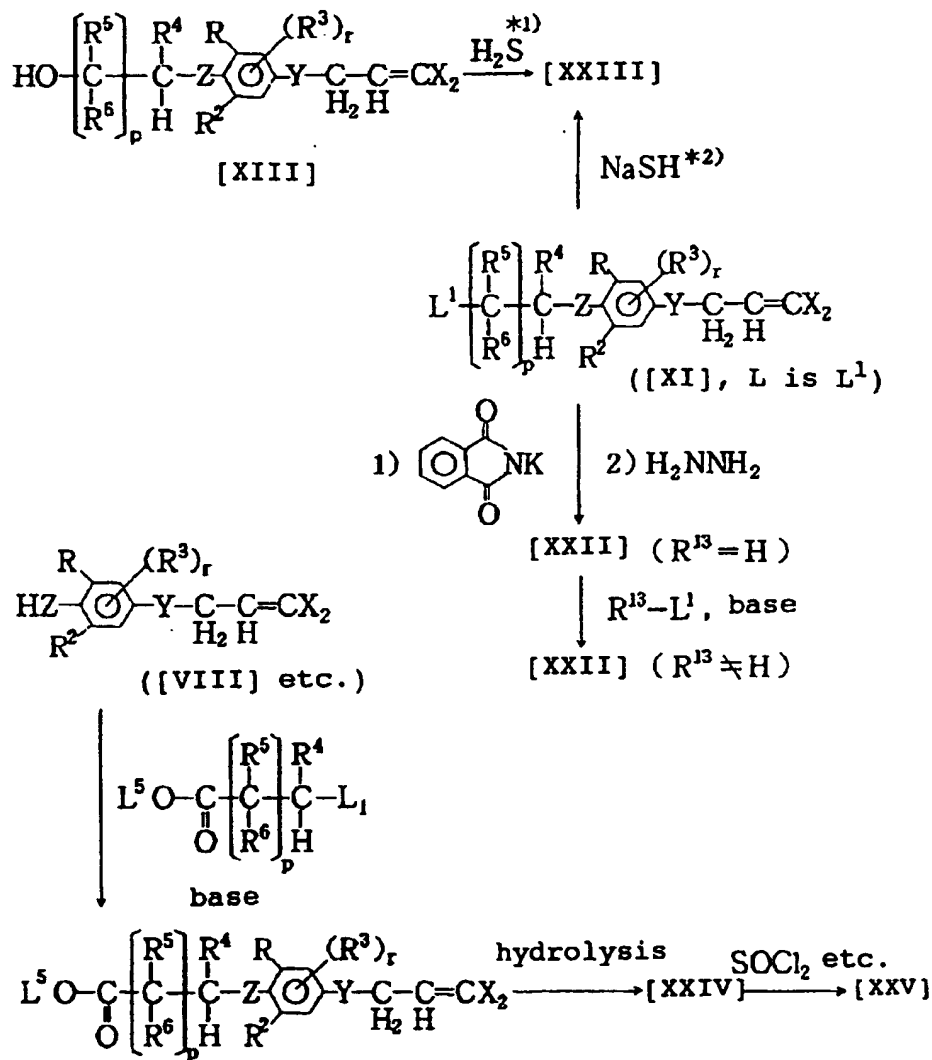
SCHEME 16 (contn'd)



wherein all the symbols are as defined above.

The compounds of general formula [XXII], [XXIII], [XXIV] or [XXV], which are used in the schemes 14 to 16, can be produced, for example, according to the following scheme 17:

SCHEME 17



*1): e.g., R.L. Kramer et al., J. Am. Chem. Soc., 43, 880 (1921).

*2): e.g., L.M. Ellis et al., J. Am. Chem. Soc., 54, 1674 (1932).

wherein all the symbols are as defined above.

The present compounds are satisfactorily effective for the control of various noxious insects, mites and ticks, examples of which are as follows:

Hemiptera:

Delphacidae such as *Laodelphax striatellus*, *Nilaparvata lugens* and *Sogatella furcifera*, *Deltocephalidae* such as *Nephotettix cincticeps* and *Nephotettix virescens*,
5 *Aphididae*, *Pentatomidae*, *Aleyrodidae*, *Coccidae*, *Tingidae*, *Psyllidae*, etc.

Lepidoptera:

Pyalidae such as *Chilo suppressalis*, *Cnaphalocrocis medinalis*, *Ostrinia nubilalis*, *Parapediasia teterrella*, *Notarcha derogata* and *Plodia interpunctella*, *Noctuidae*
10 such as *Spodoptera litura*, *Spodoptera exigua*, *Spodoptera littoralis*, *Pseudaleia separata*,
Mamestra brassicae, *Agrotis ipsilon*, *Trichoplusia* spp., *Heliothis* spp., *Helicoverpa* spp.
and *Earias* spp., *Pieridae* such as *Pieris rapae crucivora*, *Tortricidae* such as *Adoxophyes*
spp., *Carposinidae* such as *Grapholita molesta*, *Cydia pomonella* and *Carposina niponensis*,
15 *Lyonetiidae* such as *Lyonetia* spp., *Gracillariidae* such as *Lithocolletis ringoniella*,
Lymantriidae such as *Lymantria* spp. and *Euproctis* spp., *Yponomeutidae* such as
Plutella xylostella, *Gelechiidae* such as *Pectinophora gossypiella*, *Arctiidae* such as
Hyphantria cunea, *Tineidae* such as *Tinea translucens* and *Tineola bisselliella*, etc.

Diptera:

Culex such as *Culex pipiens pallens* and *Cules tritaeniorhynchus*, *Aedes* such
20 as *Aedes aegypti* and *Aedes albopictus*, *Anopheles* such as *Anophelinae sinensis*,
Chironomidae, *Muscidae* such as *Musca domestica* and *Muscina stabulans*, *Calliphoridae*,
Sarcophagidae, *Fannia canicularis*, *Anthomyiidae* such as *Hylemya Platura* and *Hylemya antiqua*,
Trypetidae, *Drosophilidae*, *Psychodidae*, *Tabanidae*, *Simuliidae*, *Stomoxysinae*,
Agromyzidae, etc.

25 Coleoptera:

Diabrotica such as *Diabrotica virgifera* and *Diabrotica undecimpunctata*,
Scarabaeidae such as *Anomala cuprea* and *Anomala rufocuprea*, *Curculionidae* such as
Sitophilus oryzae, *Lissorhoptrus oryzophilus* and *Callosobruchus chinensis*, *Tenebrio-*

nidae such as *Tenebrio molitor* and *Tribolium castaneum*, Chrysomelidae such as *Phyllotreta striolata* and *Aulacophora femoralis*, Anobiidae, Epilachna spp. such as *Epilachna vigintioctopunctata*, Lyctidae, Bostrychidae, Cerambycidae, Paederus fuscipes, etc.

5 Dictyoptera:

Blattella germanica, *Periplaneta fuliginosa*, *Periplaneta americana*, *Periplaneta brunnea*, *Blatta orientalis*, etc.

Thysanoptera:

Thrips palmi, *Thrips hawaiiensis*, etc.

10 Hymenoptera:

Formicidae, *Vespidae*, *Bethylidae*, *Tenthredinidae* such as *Athalia rosae japonensis*, etc.

Orthoptera:

Gryllotalpidae, *Acrididae*, etc.

15 Siphonaptera:

Pulex irritans etc.

Anoplura:

Pediculus humanus capitis, *Phthirus pubis*, etc.

Isoptera (termites):

20 *Reticulitermes speratus*, *Coptotermes formosanus*, etc.

Acarina:

plant parasitic *Tetranychidae* such as *Tetranychus urticae*, *Panonychus citri*, *Tetranychus cinnabarinus* and *Panonychus ulmi*, animal parasitic Ixodidae such as *Boophilus microphus*, house dust mites, etc.

25 The present compounds are also effective for the control of various noxious insects, mites and ticks having resistance to conventional insecticides and acaricides.

When the present compounds are used as active ingredients of insecticidal/-acaricidal agents, they may be used as such without any addition of other ingredients.

The present compounds are, however, usually formulated into dosage forms such as oil sprays, emulsifiable concentrates, wettable powders, flowable concentrates, granules, dusts, aerosols, fumigants (foggings) and poison baits. These dosage forms are usually prepared by mixing the present compounds with solid carriers, liquid carriers, gaseous carriers or baits, and if necessary, adding surfactants and other auxiliaries used for formulation.

Each of the dosage forms usually contains at least one of the present compounds as an active ingredient in an amount of 0.01% to 95% by weight.

Examples of the solid carrier to be used for formulation may include fine powder or granules of clay materials such as kaolin clay, diatomaceous earth, synthetic hydrated silicon oxide, bentonite, Fubasami clay and acid clay; various kinds of talc, ceramics and other inorganic minerals such as sericite, quartz, sulfur, active carbon, calcium carbonate and hydrated silica; and chemical fertilizers such as ammonium sulfate, ammonium phosphate, ammonium nitrate, urea and ammonium chloride.

Examples of the liquid carrier may include water; alcohols such as methanol and ethanol; ketones such as acetone and methyl ethyl ketone; aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene and methylnaphthalene; aliphatic hydrocarbons such as hexane, cyclohexane, kerosine and gas oil; esters such as ethyl acetate and butyl acetate; nitriles such as acetonitrile and isobutyronitrile; ethers such as diisopropyl ether and dioxane; acid amides such as N,N-dimethylformamide and N,N-dimethylacetamide; halogenated hydrocarbons such as dichloromethane, trichloroethane and carbon tetrachloride; dimethyl sulfoxide; and vegetable oils such as soybean oil and cottonseed oil.

Examples of the gaseous carrier or propellant may include flon gas, butane gas, LPG (liquefied petroleum gas), dimethyl ether and carbon dioxide.

Examples of the surfactant may include alkyl sulfates, alkyl sulfonates, alkyl arylsulfonates, alkyl aryl ethers and their polyoxyethylene derivatives, polyethylene glycol ethers, polyhydric alcohol esters and sugar alcohol derivatives.

Examples of the auxiliaries used for formulation, such as fixing agents or dispersing agents, may include casein, gelatin, polysaccharides such as starch, gum arabic, cellulose derivatives and alginic acid, lignin derivatives, bentonite, sugars, and synthetic water-soluble polymers such as polyvinyl alcohol, polyvinyl pyrrolidone and polyacrylic acid.

Examples of the stabilizer may include PAP (isopropyl acid phosphate), BHT (2,6-di-tert-butyl-4-methylphenol), BHA (mixtures of 2-tert-butyl-4-methoxyphenol and 3-tert-butyl-4-methoxyphenol), vegetable oils, mineral oils, surfactants, fatty acids and their esters.

Examples of the base material to be used in the poison baits may include bait materials such as grain powder, vegetable oils, sugars and crystalline cellulose; antioxidants such as dibutylhydroxytoluene and nordihydroguaiaretic acid; preservatives such as dehydroacetic acid; substances for preventing erroneous eating, such as red pepper powder, attractant flavors such as cheese flavor or onion flavor.

The dosage forms thus obtained are used as such or after diluted with water. The dosage forms may also be used in combination with other insecticides, nematocides, acaricides, bactericides, fungicides, herbicides, plant growth regulators, synergists, fertilizers, soil conditioners and/or animal feed under non-mixing conditions or pre-mixing conditions.

Examples of the insecticide, nematocide and/or acaricide which can be used may include organophosphorus compounds such as Fenitrothion [O,O-dimethyl O-(3-methyl-4-nitrophenyl)phosphorothioate], Fenthion [O,O-dimethyl O-(3-methyl-4-(methylthio)phenyl)phosphorothioate], Diazinon [O,O-diethyl-O-2-isopropyl-6-methylpyrimidin-4-ylphosphorothioate], Chlorpyrifos [O,O-diethyl-O-3,5,6-trichloro-2-pyridylphosphorothioate], Acephate [O,S-dimethylacetylphosphoramidothioate], Methidathion [S-2,3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-ylmethyl O,O-dimethylphosphorodithioate], Disulfoton [O,O-diethyl S-2-ethylthioethylphosphorothioate], DDVP [2,2-dichlorovinyl-dimethylphosphate], Sulprofos [O-ethyl O-4-(methylthio)phenyl S-propyl phosphorodi-

- thioate], Cyanophos [O-4-cyanophenyl O,O-dimethylphosphorothioate], Dioxabenzofos [2-methoxy-4H-1,3,2-benzodioxaphosphinine-2-sulfide], Dimethoate [O,O-dimethyl-S-(N-methylcarbamoylmethyl)dithiophosphate], Phenthoate [ethyl 2-dimethoxyphosphinothioylthio(phenyl)acetate], Malathion [diethyl(dimethoxyphosphinothioylthio)succinate],
- 5 Trichlorfon [dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate], Azinphos-methyl [S-3,4-dihydro-4-oxo-1,2,3-benzotriazin-3-ylmethyl O,O-dimethylphosphorodithioate], Monocrotophos [dimethyl (E)-1-methyl-2-(methylcarbamoyl)vinylphosphate], Ethion [O,O,O',O'-tetraethyl S,S'-methylenebis(phosphorodithioate)] and Profenofos [O-4-bromo-2-chlorophenyl O-ethyl S-propyl phosphorothioate]; carbamate compounds such
- 10 as BPMC [2-sec-butylphenylmethylcarbamate], Benfuracarb [ethyl N-[2,3-dihydro-2,2-dimethylbenzofuran-7-yloxy carbonyl(methyl)aminothio]-N-isopropyl-β-alaninate], Propoxur [2-isopropoxyphenyl N-methylcarbamate], Carbosulfan [2,3-dihydro-2,2-dimethyl-7-benzo[b]furanyl N-dibutylaminothio-N-methylcarbamate], Carbaril [1-naphthyl-N-methylcarbamate], Methomyl [S-methyl-N-[(methylcarbamoyl)oxy]thioacetimidate],
- 15 Ethiofencarb [2-(ethylthiomethyl)phenylmethylcarbamate], Aldicarb [2-methyl-2-(methylthio)propanaldehyde O-methylcarbamoyloxime], Oxamyl [N,N-dimethyl-2-methylcarbamoyloxyimino-2-(methylthio)acetamide], Fenothiocarb [S-(4-phenoxybutyl)-N,N-dimethylthiocarbamate], Thiodicarb [3,7,9,13-tetramethyl-5,11-dioxo-2,8,14-trithia-4,7,9,12-tetraazapentadeca-3,12-diene-6,10-dione] and Alanylcab [ethyl (Z)-N-benzyl-N-
- 20 ([methyl(1-methylthioethylideneamino)oxycarbonyl)amino]thio)-β-alaninate]; pyrethroid compounds such as Etofenprox [2-(4-ethoxyphenyl)-2-methylpropyl-3-phenoxybenzyl-ether], Fenvalerate [(RS)-α-cyano-3-phenoxybenzyl (RS)-2-(4-chlorophenyl)-3-methylbutyrate], Esfenvalerate [(S)-α-cyano-3-phenoxybenzyl (S)-2-(4-chlorophenyl)-3-methylbutyrate], Fenprothrin [(RS)-α-cyano-3-phenoxybenzyl 2,2,3,3-tetramethylcyclopropanecarboxylate], Cypermethrin [(RS)-α-cyano-3-phenoxybenzyl (1RS,3RS)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate], Permethrin [3-phenoxybenzyl (1RS,3RS)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate], Cyhalothrin [(RS)-α-cyano-3-phenoxybenzyl (Z)-(1RS)-cis-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-di-

methylcyclopropanecarboxylate], Deltamethrin [(S)- α -cyano-m-phenoxybenzyl (1R,3R)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate], Cycloprothrin [(RS)- α -cyano-3-phenoxybenzyl (RS)-2,2-dichloro-1-(4-ethoxyphenyl)cyclopropanecarboxylate], Fluvalinate [α -cyano-3-phenoxybenzyl N-(2-chloro- α,α,α -trifluoro-p-tolyl)-D-valinate],
 5 Bifenthrin [2-methylbiphenyl-3-ylmethyl] (Z)-(1RS)-cis-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate], Acrinathrin [(S)- α -cyano-(3-phenoxyphenyl)methyl [1R-{1 α (S*),3 α (Z)}]-2,2-dimethyl-3-[3-oxo-3-(2,2,2-trifluoro-1-(trifluoromethyl)ethoxy-1-propenyl)cyclopropanecarboxylate], 2-methyl-2-(4-bromodifluoromethoxyphenyl)propyl (3-phenoxybenzyl) ether, Traromethrin [(S)- α -cyano-3-phenoxy-
 10 benzyl (1R,3R)-3-[(1'RS)(1',1',2',2'-tetrabromoethyl)]-2,2-dimethylcyclopropanecarboxylate] and Silafluofen [4-ethoxyphenyl [3-(4-fluoro-3-phenoxyphenyl)propyl]dimethylsilane]; thiadiazine derivatives such as Buprofezin [2-tert-butylimino-3-isopropyl-5-phenyl-1,3,5-thiadiazin-4-one]; nitroimidazolidine derivatives such as Imidacloprid [1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylidenamine]; Nereistoxin deriva-
 15 tives such as Cartap [S,S'-(2-dimethylaminotrimethylene)bis(thiocarbamate)], Thio-cyclam [N,N-dimethyl-1,2,3-trithian-5-ylamine] and Bensultap [S,S'-2-dimethylamino-trimethylene di(benzenethiosulfonate)]; N-cyanoamidine derivatives such as acetamiprid [N-cyano-N'-methyl-N'-(6-chloro-3-pyridylmethyl)acetamidine]; chlorinated hydro-
 carbon compounds such as Endosulfan [6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexa-
 20 hydro-6,9-methano-2,4,3-benzodioxathiepinoxide], γ -BHC [1,2,3,4,5,6-hexachlorocyclohexane] and Kelthane [1,1-bis(chlorophenyl)-2,2,2-trichloroethanol]; benzoylphenyl-urea compounds such as Chlorfluazuron [1-(3,5-dichloro-4-(3-chloro-5-trifluoromethylpyridin-2-yloxy)phenyl)-3-(2,6-difluorobenzoyl)urea], Teflubenzuron [1-(3,5-dichloro-2,4-difluorophenyl)-3-(2,6-difluorobenzoyl)urea] and Fulphenoxron [1-(4-(2-chloro-4-tri-
 25 fluoromethylphenoxy)-2-fluorophenyl)-3-(2,6-difluorobenzoyl)urea]; formamidine derivatives such as Amitraz [N,N'-[(methylimino)dimethylidene]-di-2,4-xylidine] and Chlordimeform [N'-(4-chloro-2-methylphenyl)-N,N-dimethylmethanimidamide]; thiourea derivatives such as Diafenthuron [N-(2,6-diisopropyl-4-phenoxyphenyl)-N'-tert-butylcarbo-

diimide]; Bromopropylate [isopropyl 4,4'-dibromobenzylate], Tetradifon [4-chlorophenyl 2,4,5-trichlorophenylsulfone], Quinomethionate [S,S-6-methylquinoxaline-2,3-diylthio-carbonate], Propargite [2-(4-tert-butylphenoxy)cyclohexyl prop-2-yl sulfite], Fenbutatin oxide [bis[tris(2-methyl-2-phenylpropyl)tin]oxide], Hexythiazox [(4RS,5RS)-5-(4-chloro-phenyl)-N-chlorohexyl-4-methyl-2-oxo-1,3-thiazolidine-3-carboxamide], Chlofentezine [3,6-bis(2-chlorophenyl)-1,2,4,5-tetrazine], Pyridaben [2-tert-butyl-5-(4-tert-butylbenzyl-thio)-4-chloropyridazin-3(2H)-one], Fenpyroximate [tert-butyl (E)-4-[(1,3-dimethyl-5-phenoxy-pyrazol-4-yl)methyleneaminooxymethyl]benzoate], Tebfenpyrad [N-4-tert-butyl-benzyl)-4-chloro-3-ethyl-1-methyl-5-pyrazolecarboxamide], polynactin complexes includ-
10 ing tetranactin, dinactin and trinactin; Milbemectin, Avermectin, Ivermectin, Azadilactin [AZAD], Pyrimidifen [5-chloro-N-[2-{4-(2-ethoxyethyl)-2,3-dimethylphenoxy}ethyl]-6-ethylpyrimidin-4-amine], Chlorfenapyr [4-bromo-2-(4-chlorophenyl)-1-ethoxymethyl-5-trifluoromethylpyrrole-3-carbonitrile], Tebfenozide [N-tert-butyl-N'-(4-ethylbenzoyl)-3,5-dimethylbenzohydrazide] and phenylpyrazole derivatives.

15 When the present compounds are used as active ingredients of insecti-
cidal/acaricidal agents for agriculture, the application amount thereof is usually in the
range of 0.1 to 100 g per 10 ares. In the case of emulsifiable concentrates, wettable
powders and flowable concentrates, which are used after diluted with water, the
application concentration thereof is usually in the range of 1 to 10,000 ppm. In the case
20 of granules and dusts, they are applied as such without any dilution. When the present
compounds are used as active ingredients of insecticidal/acaricidal agents for epidemic
prevention, they are formulated into dosage forms such as emulsifiable concentrates,
wettable powders and flowable concentrates, which are applied after diluted with water to
a typical concentration of 0.1 to 500 ppm; or they are formulated into dosage forma such
25 as oil sprays, aerosols, fumigants and poisonous baits, which are applied as such without
any dilution.

The application amount and application concentration may vary with the
conditions including types of dosage forms, application time, place and method, kinds of

noxious insects, mites and ticks, and degree of damage, and they can be increased or decreased without limitation to the above range.

The present invention will be further illustrated by the following production examples, formulation examples and test examples; however, the present invention is not
5 limited to these examples.

The following are production examples for the present compounds according to various production processes.

Production Example 1

Production of compound (3) by production process F

10 A reaction vessel was charged with 0.70 g of 3,5-dichloro-4-(4-bromobutyl-oxy)-1-(3,3-dichloro-2-propenyloxy)benzene, 0.34 g of 4-(1-piperidinylcarbonyl)phenol, 0.25 g of potassium carbonate and 10 ml of N,N-dimethylformamide. After stirring at room temperature for 24 hours, the reaction mixture was poured into water and extracted twice with 30 ml of diethyl ether. The ether layers were combined, washed with water,
15 dried over magnesium sulfate and then concentrated to give a crude product. The crude product was subjected to silica gel chromatography, which afforded 0.66 g of 3,5-dichloro-4-(4-(4-(1-piperidinylcarbonyl)phenoxy)butyloxy)-1-(3,3-dichloro-2-propenyl-oxy)benzene (yield, 73%), $n_D^{22.5}$ 1.5751.

Production Example 2

20 Production of compound (11) by production process H

To a mixture of 0.47 g of 4-(3-(2,6-dichloro-4-(3,3-dichloro-2-propenyloxy)-phenoxy)propyloxy)benzoic acid [intermediate compound 2) prepared in Intermediate Production Example 1 below], 0.10 g of di(2-propenyl)amine and 10 ml of chloroform was added 0.20 g of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (WSC) hydro-
25 chloride with stirring. After stirring at room temperature for 24 hours, the reaction mixture was concentrated. The residue was subjected to silica gel chromatography, which afforded 0.45 g of 3,5-dichloro-4-(3-(4-(N,N-di(2-propenyl)carbamoyl)phenoxy)-propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene (yield, 83%), $n_D^{27.0}$ 1.5612.

Production Example 3

Production of compound (16) by production process I

To a solution of 2.67 g of triphosgene dissolved in 50 ml of toluene was added 2.03 g of 3,5-dichloro-4-(4-(4-aminophenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene [intermediate compound 10) prepared in Intermediate Production Example 2] with stirring under ice cooling. The reaction mixture was heated under reflux for 3 hours with stirring and then concentrated to give a crude product of 4-(4-(2,6-dichloro-4-(3,3-dichloro-2-propenyloxy)phenoxy)butyloxy)phenylisocyanate. To this crude product was added tetrahydrofuran to give a 15 ml solution. A 5 ml portion of this solution was slowly added dropwise to a reaction vessel containing a mixture of 0.17 g of di-n-propylamine and 10 ml of tetrahydrofuran with stirring under ice cooling. After stirring at room temperature for 24 hours, the reaction mixture was concentrated. The residue was subjected to silica gel chromatography, which afforded 0.77 g of 3,5-dichloro-4-(4-(4-(N,N-dipropylureido)phenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)-benzene (yield, 89%), m.p. 93.5°C.

Production Example 4

Production of compound (27) by production process A

A reaction vessel is charged with 0.43 g of 3-ethyl-5-methyl-4-(3-(4-(N,N-dipropylcarbamoyl)phenoxy)propyloxy)phenol, 0.16 g of 1,1,3-trichloropropene, 0.15 g of potassium carbonate and 10 ml of N,N-dimethylformamide. After stirring at room temperature for 24 hours, the reaction mixture is poured into water and extracted twice with ethyl acetate. The ethyl acetate layers are combined, washed with water, dried over magnesium sulfate and then concentrated. The residue is subjected to silica gel chromatography, which affords 3-ethyl-5-methyl-4-(3-(4-(N,N-dipropylcarbamoyl)phenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene.

The following are specific examples of the present compounds with their compound numbers and physical properties, if measured.

(1) 3,5-Dichloro-4-(2-(4-(1-piperidinylcarbonyl)phenoxy)ethyloxy)-1-

- (3,3-dichloro-2-propenyloxy)benzene $n_D^{22.5}$ 1.5821
- (2) 3,5-Dichloro-4-(3-(4-(1-piperidinylcarbonyl)phenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene $n_D^{22.8}$ 1.5655
- (3) 3,5-Dichloro-4-(4-(4-(1-piperidinylcarbonyl)phenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene $n_D^{22.5}$ 1.5713
- 5 (4) 3,5-Dichloro-4-(3-(3-(1-piperidinylcarbonyl)phenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene $n_D^{25.0}$ 1.5574
- (5) 3,5-Dichloro-4-(3-(2-(1-piperidinylcarbonyl)phenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene $n_D^{25.0}$ 1.5669
- 10 (6) 3,5-Dichloro-4-(3-(4-(1-pyrrolidinylcarbonyl)phenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene $n_D^{22.5}$ 1.5751
- (7) 3,5-Dichloro-4-(3-(4-(3-pyrrolin-1-ylcarbonyl)phenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene $n_D^{24.5}$ 1.5762
- (8) 3,5-Dichloro-4-(3-(4-(N,N-dipropylcarbamoyl)phenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene $n_D^{22.7}$ 1.5184
- 15 (9) 3,5-Dichloro-4-(3-(4-(N,N-dibutylcarbamoyl)phenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene $n_D^{25.0}$ 1.5378
- (10) 3,5-Dichloro-4-(3-(4-(N,N-dipropylcarbamoyl)phenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene $n_D^{25.0}$ 1.5430
- 20 (11) 3,5-Dichloro-4-(3-(4-(N,N-di(2-propenyl)carbamoyl)phenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene $n_D^{27.0}$ 1.5612
- (12) 3,5-Dichloro-4-(3-(4-(N-propylcarbamoyl)phenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene m.p. 85.1°C
- (13) 3,5-Dichloro-4-(5-(4-(N,N-dipropylcarbamoyl)phenoxy)pentyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene
- 25 (14) 3,5-Dichloro-4-(3-(4-(N,N-dipropylcarbamoyl)phenoxy)propyloxy)-1-(3,3-dibromo-2-propenyloxy)benzene
- (15) 3,5-Dichloro-4-(3-(4-(N,N-di(2-propynyl)carbamoyl)phenoxy)propyl-

oxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(16) 3,5-Dichloro-4-(4-(4-(N,N-dipropylureido)phenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene m.p. 93.5°C

(17) 3,5-Dichloro-4-(4-(4-(N-propylureido)phenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene m.p. 115.1°C

(18) 3,5-Dichloro-4-(4-(4-(N,N-dipropylcarbamoyloxy)phenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(19) 3,5-Dichloro-4-(4-(4-(N-propylcarbamoyloxy)phenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(20) 3,5-Dichloro-4-(4-(4-(N,N-dipropylcarbamoyl)phenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(21) 3,5-Dichloro-4-(4-(4-(N,N-di(2-propenyl)carbamoyl)phenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(22) 3,5-Dichloro-4-(4-(4-(N,N-di(2-propynyl)carbamoyl)phenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(23) 3,5-Diethyl-4-(3-(4-(N,N-dipropylcarbamoyl)phenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(24) 3,5-Diethyl-4-(3-(4-(N,N-di(2-propenyl)carbamoyl)phenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(25) 3,5-Diethyl-4-(3-(4-(N,N-di(2-propynyl)carbamoyl)phenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(26) 3,5-Diethyl-4-(3-(4-(1-piperidinylcarbonyl)phenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(27) 3-Ethyl-5-methyl-4-(3-(4-(N,N-dipropylcarbamoyl)phenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(28) 3-Ethyl-5-methyl-4-(3-(4-(N,N-di(2-propenyl)carbamoyl)phenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(29) 3-Ethyl-5-methyl-4-(3-(4-(N,N-di(2-propynyl)carbamoyl)phenoxy)-

propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(30) 3-Ethyl-5-methyl-4-(3-(4-(1-piperidinylcarbonyl)phenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(31) 3,5-Diethyl-4-(4-(4-(N,N-dipropylcarbamoyl)phenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(32) 3,5-Diethyl-4-(4-(4-(N,N-di(2-propenyl)carbamoyl)phenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(33) 3,5-Diethyl-4-(4-(4-(N,N-di(2-propynyl)carbamoyl)phenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(34) 3,5-Diethyl-4-(4-(4-(1-piperidinylcarbonyl)phenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(35) 3-Ethyl-5-methyl-4-(4-(4-(N,N-dipropylcarbamoyl)phenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(36) 3-Ethyl-5-methyl-4-(4-(4-(N,N-di(2-propenyl)carbamoyl)phenoxy)-butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(37) 3-Ethyl-5-methyl-4-(4-(4-(N,N-di(2-propynyl)carbamoyl)phenoxy)-butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

(38) 3-Ethyl-5-methyl-4-(4-(4-(1-piperidinylcarbonyl)phenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene

The following is a production example for the intermediates of the general formula [XIV] and/or [III].

Intermediate Production Example 1

Production of intermediate compound 2)

A reaction vessel was charged with 4.91 g of 3,5-dichloro-4-(3-bromopropyl-oxy)-1-(3,3-dichloro-2-propenyloxy)benzene, 1.83 g of methyl 4-hydroxybenzoate, 1.82 g of potassium carbonate and 50 ml of N,N-dimethylformamide. After stirring at room temperature for 24 hours, the reaction mixture was poured into water and extracted twice with 100 ml of diethyl ether. The ether layers were combined, washed with water,

dried over magnesium sulfate and then concentrated to give a crude product. The crude product was subjected to silica gel chromatography, which afforded 5.58 g of methyl 4-(3-(2,6-dichloro-4-(3,3-dichloro-2-propenyloxy)phenoxy)propyloxy)benzoate (yield, 96%), $n_D^{22.7}$ 1.5519.

- 5 To a mixture of 2.50 g of methyl 4-(3-(2,6-dichloro-4-(3,3-dichloro-2-propenyloxy)phenoxy)propyloxy)benzoate and 20 ml of methanol was added a solution of 0.41 g of potassium hydroxide dissolved in 4 ml of water. The reaction mixture was heated under reflux for 12 hours with stirring and then acidified by the addition of diluted hydrochloric acid, followed by concentration. To the residue was added water, and the
- 10 mixture was extracted twice with 30 ml of ethyl acetate. The ethyl acetate layers were combined, washed with water, dried over magnesium sulfate and then concentrated to give crude crystals. The crude crystals were washed with hexane, which afforded 1.90 g of 4-(3-(2,6-dichloro-4-(3,3-dichloro-2-propenyloxy)phenoxy)propyloxy)benzoic acid (yield, 78%), m.p. 137.5°C.

- 15 The following are some specific examples of the intermediates of general formula [XIV] and/or [III] with their compound numbers and physical properties, if measured.

- | | | | |
|----|----|---|--------------|
| | 1) | 4-(2-(2,6-Dichloro-4-(3,3-dichloro-2-propenyloxy)phenoxy)ethyloxy)-benzoic acid | |
| 20 | 2) | 4-(3-(2,6-Dichloro-4-(3,3-dichloro-2-propenyloxy)phenoxy)propyloxy)benzoic acid | m.p. 137.5°C |
| | 3) | 4-(4-(2,6-Dichloro-4-(3,3-dichloro-2-propenyloxy)phenoxy)butyloxy)benzoic acid | |
| | 4) | 4-(5-(2,6-Dichloro-4-(3,3-dichloro-2-propenyloxy)phenoxy)pentyloxy)benzoic acid | |
| 25 | 5) | 3-(3-(2,6-Dichloro-4-(3,3-dichloro-2-propenyloxy)phenoxy)propyloxy)benzoic acid | |
| | 6) | 2-(3-(2,6-Dichloro-4-(3,3-dichloro-2-propenyloxy)phenoxy)propyloxy)benzoic acid | |

oxy)benzoic acid

7) 4-(3-(2,6-Dichloro-4-(3,3-dibromo-2-propenyloxy)phenoxy)propyloxy)benzoic acid

The isocyanate compounds of the general formula [XVI] can be produced from the corresponding aniline compounds. The following is a production example for the aniline intermediate compounds.

Intermediate Production Example 2

Production of intermediate compound 10)

A reaction vessel was charged with 6.34 g of 3,5-dichloro-4-(4-bromobutyl-oxy)-1-(3,3-dichloro-2-propenyloxy)benzene, 2.27 g of 4-acetamidophenol, 2.28 g of potassium carbonate and 50 ml of N,N-dimethylformamide. After stirring at room temperature for 24 hours, the reaction mixture was poured into water and extracted twice with 50 ml of ethyl acetate. The ethyl acetate layers were combined, washed with water, dried over magnesium sulfate and then concentrated to give crude crystals. The crude crystals were washed with hexane, which afforded 4.70 g of 3,5-dichloro-4-(4-(4-acetamidophenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene (yield, 64%), m.p. 135.8°C.

To a mixture of 4.44 g of 3,5-dichloro-4-(4-(4-acetamidophenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene, 120 ml of methanol and 30 ml of mixture was added 20 ml of concentrated hydrochloric acid. The reaction mixture was heated under reflux for 6 hours with stirring and then concentrated. To the residue was added an aqueous solution of sodium hydrogencarbonate, and the mixture was extracted twice with 100 ml of ethyl acetate. The ethyl acetate layers were combined, washed with water, dried over magnesium sulfate and then concentrated to give a crude product. The crude product was subjected to silica gel chromatography, which afforded 3.84 g of 3,5-dichloro-4-(4-(4-aminophenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene (yield, 95%), $n_D^{22.5}$ 1.5816.

The following are some specific examples of the above aniline intermediate

compounds with their compound numbers and physical properties, if measured.

- 8) 3,5-Dichloro-4-(2-(4-aminophenoxy)ethyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene
- 9) 3,5-Dichloro-4-(3-(4-aminophenoxy)propyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene
- 10) 3,5-Dichloro-4-(4-(4-aminophenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene $n_D^{22.5}$ 1.5816
- 11) 3,5-Dichloro-4-(5-(4-aminophenoxy)pentyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene
- 12) 3,5-Dichloro-4-(4-(3-aminophenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene
- 13) 3,5-Dichloro-4-(4-(2-aminophenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)phenoxy)benzene

The following are production examples for the compounds of the general formula [IV], which are intermediates for the production of the present compounds.

Intermediate Production Example 3

Production of intermediate compound 21)

A reaction vessel was charged with 1.07 g of hydroquinone monobenzyl ether and 500 ml of carbon tetrachloride, to which a solution of 1.01 g of t-butyl hypochlorite dissolved in 10 ml of carbon tetrachloride was slowly added dropwise with stirring under ice cooling. After 24 hours, the reaction mixture was poured into water, and the organic (carbon tetrachloride) layer was separated, washed with water, dried over anhydrous magnesium sulfate and then concentrated to give a crude product. The crude product was subjected to silica gel chromatography, which afforded 0.85 g of 2,6-dichloro-4-benzyloxyphenol (yield, 59%).

A reaction vessel was charged with 8.08 g of 1,3-dibromopropane, 3.04 g of potassium carbonate and 100 ml of N,N-dimethylformamide, to which a solution of 5.38 g of 2,6-dichloro-4-benzyloxyphenol dissolved in 50 ml of N,N-dimethylformamide

was added dropwise at room temperature over 2 hours. After stirring at room temperature for 1 hour, the reaction mixture was filtered through celite. The filtrate was poured into water and extracted twice with diethyl ether. The ether layers were combined, washed with water, dried over anhydrous magnesium sulfate and then concentrated to give a crude product. The crude product was subjected to silica gel chromatography, which afforded 6.36 g of 3,5-dichloro-4-(3-bromopropoxy)-1-benzyloxybenzene (yield, 82%).

A reaction vessel was charged with 0.66 g of 4-(N,N-dipropylcarbamoyl)-phenol, 1.29 g of 3,5-dichloro-4-(3-bromopropoxy)-1-benzyloxybenzene, 0.50 of potassium carbonate and 20 ml of N,N-dimethylformamide. After stirring at 40°C for 24 hours, the reaction mixture was poured into water and extracted twice with diethyl ether. The ether layers were combined, washed with water, dried over magnesium sulfate and then concentrated to give a crude product. The crude product was subjected to silica gel chromatography, which afforded 1.24 g of 3,5-dichloro-4-(3-(4-(N,N-dipropylcarbamoyl)phenoxy)propoxy)-1-benzyloxybenzene (yield, 76%), $n_D^{24.0}$ 1.5572.

A reaction vessel was charged with 1.06 g of 3,5-dichloro-4-(3-(4-(N,N-dipropylcarbamoyl)phenoxy)propoxy)-1-benzyloxybenzene and 40 ml of ethyl acetate. The air in the vessel was replaced with nitrogen gas. To the vessel was added 0.30 g of 10% palladium on carbon, and the nitrogen gas in the vessel was replaced with hydrogen gas, followed by vigorous stirring at room temperature for 2 hours. The hydrogen gas in the vessel was replaced with nitrogen gas, and the reaction mixture was filtered through celite. The filtrate was concentrated, which afforded 0.71 g of 3,5-dichloro-4-(3-(4-(N,N-dipropylcarbamoyl)phenoxy)propoxy)phenol (yield, 80%).

$^1\text{H-NMR}$ (CDCl_3/TMS) δ (ppm): 0.68-1.10 (6H, br s), 1.42-1.79 (4H, br s), 2.23 (2H, dt), 3.05-3.55 (4H, br s), 3.48 (1H, s), 4.08 (2H, t), 4.23 (2H, t), 6.56 (2H, s), 6.88 (2H, d), 7.27 (2H, d)

Intermediate Production Example 4

Production of intermediate compound 39)

A mixture of 27 g of 2-ethyl-6-methylaniline, 36 ml of concentrated sulfuric acid and 100 ml of water was stirred at 0° to 5°C, during which a solution of 16.1 g of sodium nitrite dissolved in 50 ml of water was added dropwise to the mixture. After completion of the dropwise addition, 150 g of chilled water, 1.5 g of urea and 150 g of ice were added thereto.

This aqueous solution was added dropwise to a mixture of 100 ml of sulfuric acid, 100 ml of water and 150 g of sodium sulfate heated at 135°C with stirring. At the same time as the dropwise addition, steam distillation was carried out. After completion of the dropwise addition, an aqueous solution obtained by the steam distillation was subjected to salting out with sodium chloride, dried over anhydrous magnesium sulfate and then concentrated to give a crude product. The crude product was subjected to silica gel chromatography, which afforded 16 g of 2-ethyl-6-methylphenol (yield, 59%).

Then, 16 g of 2-ethyl-6-methylphenol was dissolved in 200 ml of chloroform, to which 56.6 g of tetrabutylammonium tribromide was added in portions with stirring at 0°C. After stirring at room temperature for 1 hour, the solvent was distilled out under reduced pressure. The residue was dissolved in 300 ml of diethyl ether, washed with 10% hydrochloric acid and then water, dried over anhydrous magnesium sulfate and then concentrated to give a crude product. The crude product was subjected to silica gel chromatography, which afforded 23 g of 4-bromo-2-ethyl-6-methylphenol (yield, 92%).

To a mixture of 26 g of 4-bromo-2-ethyl-6-methylphenol, 24.8 g of benzyl bromide and 200 ml of N,N-dimethylformamide was added 21.7 g of potassium carbonate with stirring at room temperature. After stirring at room temperature for 24 hours, the reaction mixture was poured into ice water and extracted twice with 500 ml of diethyl ether. The diethyl ether layers were combined, washed with water, dried over anhydrous magnesium sulfate and then concentrated to give a crude product. The crude product was subjected to silica gel chromatography, which afforded 35.6 g of 4-bromo-2-ethyl-6-methyl-1-benzyloxybenzene (yield, 97%).

Then, 35.6 g of 4-bromo-2-ethyl-6-methyl-1-benzyloxybenzene was

dissolved in 250 ml of tetrahydrofuran, to which 69 ml of a solution of n-butyl lithium in hexane (1.69 mol/l) was added dropwise with stirring at -70°C . After further stirring at -70°C for 2 hours, a solution of 12.1 g of trimethoxyborane dissolved in 50 ml of tetrahydrofuran was added dropwise to the reaction mixture. After completion of the dropwise addition, the reaction mixture was returned to room temperature and stirred for 1 hour, which was poured into ice water, weakly acidified by the addition of 10% hydrochloric acid and extracted twice with 500 ml of diethyl ether. The ether layers were combined, washed with water, dried over anhydrous magnesium sulfate and then concentrated. To the residue was added 120 ml of toluene, to which 33 ml of 30% aqueous hydrogen peroxide solution was added dropwise with stirring under heating at 70°C . After heating under reflux for 1 hour, the reaction mixture was returned to room temperature, washed once with water, twice with 10% aqueous ammonium ferrous sulfate solution and further once with water, and the toluene layer was dried over anhydrous magnesium sulfate and then concentrated to give a crude product. The crude product was subjected to silica gel chromatography, which afforded 26.2 g of 3-ethyl-4-benzyloxy-5-methylphenol (yield, 93%).

To a mixture of 6.3 g of 4-benzyloxy-3-ethyl-5-methylphenol, 3.2 g of triethylamine and 50 ml of chloroform was added dropwise 4.0 g of benzoyl chloride with stirring at 0°C . After stirring at room temperature for 6 hours, the reaction mixture was concentrated under reduced pressure. To the residue was added 100 ml of 10% hydrochloric acid, which was extracted with 100 ml of ethyl acetate. The ethyl acetate layer was washed with 10% hydrochloric acid, aqueous sodium hydrogencarbonate solution and then saturated sodium chloride solution, dried over anhydrous magnesium sulfate and then concentrated under reduced pressure, which afforded 8.4 g of crude 4-benzyloxy-3-ethyl-5-methylphenyl benzoate (yield, 93%).

Then, 8.4 g of crude 4-benzyloxy-3-ethyl-5-methylphenylbenzoate was dissolved in 100 ml of ethyl acetate, and the solution was put in a reaction vessel. The air in the reaction vessel was replaced with nitrogen gas. To the vessel was added 0.5 g of

10% palladium on carbon, and the nitrogen gas in the vessel was replaced with hydrogen gas, followed by vigorous stirring at room temperature for 24 hours. The hydrogen gas in the vessel was replaced with nitrogen gas, and the reaction mixture was filtered through celite. The filtrate was concentrated under reduced pressure, which afforded 5.9 g of
5 2-ethyl-6-methyl-4-benzoyloxyphenol (yield, 95%).

A reaction vessel is charged with 0.24 g of 2-ethyl-6-methyl-4-benzoyloxyphenol, 0.34 g of 4-(N,N-dipropylcarbamoyl)-1-(3-bromopropoxy)benzene, 0.15 g of potassium carbonate and 10 ml of N,N-dimethylformamide. After stirring at room temperature for 24 hours, the reaction mixture is poured into water and extracted twice
10 with ethyl acetate. The ethyl acetate layers are combined, washed with water, dried over magnesium sulfate and then concentrated. The residue is subjected to silica gel chromatography, which affords 3-ethyl-5-methyl-4-(3-(4-(N,N-dipropylcarbamoyl)phenoxy)propyloxy)phenyl benzoate.

To a solution of 0.52 g of 3-ethyl-5-methyl-4-(3-(4-N,N-dipropylcarbamoyl)-
15 phenoxypropyloxy)phenyl benzoate dissolved in 10 ml of methanol is added a solution of 0.072 g of potassium hydroxide dissolved in 0.70 g of water. The reaction mixture is stirred at room temperature for 1 hour and then acidified by the addition of diluted hydrochloric acid, followed by concentration. To the residue is added water, and the mixture is extracted twice with ethyl acetate. The ethyl acetate layers are combined, washed with
20 water, dried over magnesium sulfate and then concentrated. The residue is subjected to silica gel chromatography, which affords 3-ethyl-5-methyl-4-(3-(4-(N,N-dipropylcarbamoyl)phenoxy)propyloxy)phenol.

The following are some specific examples of the compounds of the general formula [IV], which are intermediates for the production of the compounds of the present
25 invention.

14) 3,5-Dichloro-4-(2-(4-(1-piperidinylcarbonyl)phenoxy)ethyloxy)phenol

15) 3,5-Dichloro-4-(3-(4-(1-piperidinylcarbonyl)phenoxy)propyloxy)-
phenol

- 16) 3,5-Dichloro-4-(4-(4-(1-piperidinylcarbonyl)phenoxy)butyloxy)phenol
- 17) 3,5-Dichloro-4-(3-(3-(1-piperidinylcarbonyl)phenoxy)propyloxy)-
phenol
- 18) 3,5-Dichloro-4-(3-(2-(1-piperidinylcarbonyl)phenoxy)propyloxy)-
5 phenol
- 19) 3,5-Dichloro-4-(3-(4-(1-pyrrolidinylcarbonyl)phenoxy)propyloxy)-
phenol
- 20) 3,5-Dichloro-4-(3-(4-(3-pyrrolin-1-ylcarbonyl)phenoxy)propyloxy)-
phenol
- 10 21) 3,5-Dichloro-4-(3-(4-(N,N-dipropylcarbamoyl)phenoxy)propyloxy)-
phenol
- 22) 3,5-Dichloro-4-(3-(4-(N,N-diethylcarbamoyl)phenoxy)propyloxy)-
phenol
- 23) 3,5-Dichloro-4-(3-(4-(N,N-diisopropylcarbamoyl)phenoxy)propyloxy)-
15 phenol
- 24) 3,5-Dichloro-4-(3-(4-(N,N-di(2-propenyl)carbamoyl)phenoxy)propyl-
oxy)phenol
- 25) 3,5-Dichloro-4-(3-(4-(N-propylcarbamoyl)phenoxy)propyloxy)phenol
- 26) 3,5-Dichloro-4-(5-(4-(N,N-dipropylcarbamoyl)phenoxy)pentyloxy)-
20 phenol
- 27) 3,5-Dichloro-4-(3-(4-(N,N-di(2-propynyl)carbamoyl)phenoxy)propyl-
oxy)phenol
- 28) 3,5-Dichloro-4-(4-(4-(N,N-dipropylureido)phenoxy)butyloxy)phenol
- 29) 3,5-Dichloro-4-(4-(4-(N-propylureido)phenoxy)butyloxy)phenol
- 25 30) 3,5-Dichloro-4-(4-(4-(N,N-dipropylcarbamoyloxy)phenoxy)butyloxy)-
phenol
- 31) 3,5-Dichloro-4-(4-(4-(N-propylcarbamoyloxy)phenoxy)butyloxy)-
phenol

- 32) 3,5-Dichloro-4-(4-(4-(N,N-dipropylcarbamoyl)phenoxy)butyloxy)-phenol
- 33) 3,5-Dichloro-4-(4-(4-(N,N-di(2-propenyl)carbamoyl)phenoxy)butyloxy)phenol
- 5 34) 3,5-Dichloro-4-(4-(4-(N,N-di(2-propynyl)carbamoyl)phenoxy)butyloxy)phenol
- 35) 3,5-Diethyl-4-(3-(4-(N,N-dipropylcarbamoyl)phenoxy)propyloxy)-phenol
- 36) 3,5-Diethyl-4-(3-(4-(N,N-di(2-propenyl)carbamoyl)phenoxy)propyloxy)phenol
- 10 37) 3,5-Diethyl-4-(3-(4-(N,N-di(2-propynyl)carbamoyl)phenoxy)propyloxy)phenol
- 38) 3,5-Diethyl-4-(3-(4-(1-piperidinylcarbonyl)phenoxy)propyloxy)phenol
- 39) 3-Ethyl-5-methyl-4-(3-(4-(N,N-dipropylcarbamoyl)phenoxy)propyloxy)phenol
- 15 40) 3-Ethyl-5-methyl-4-(3-(4-(N,N-di(2-propenyl)carbamoyl)phenoxy)propyloxy)phenol
- 41) 3-Ethyl-5-methyl-4-(3-(4-(N,N-di(2-propynyl)carbamoyl)phenoxy)propyloxy)phenol
- 20 42) 3-Ethyl-5-methyl-4-(3-(4-(1-piperidinylcarbonyl)phenoxy)propyloxy)-phenol
- 43) 3,5-Diethyl-4-(4-(4-(N,N-dipropylcarbamoyl)phenoxy)butyloxy)-phenol
- 44) 3,5-Diethyl-4-(4-(4-(N,N-di(2-propenyl)carbamoyl)phenoxy)butyloxy)-phenol
- 25 45) 3,5-Diethyl-4-(4-(4-(N,N-di(2-propynyl)carbamoyl)phenoxy)butyloxy)-phenol
- 46) 3,5-Diethyl-4-(4-(4-(1-piperidinylcarbonyl)phenoxy)butyloxy)phenol

- 47) 3-Ethyl-5-methyl-4-(4-(4-(N,N-dipropylcarbamoyl)phenoxy)butyloxy)-phenol
- 48) 3-Ethyl-5-methyl-4-(4-(4-(N,N-di(2-propenyl)carbamoyl)phenoxy)-butyloxy)phenol
- 5 49) 3-Ethyl-5-methyl-4-(4-(4-(N,N-di(2-propynyl)carbamoyl)phenoxy)-butyloxy)phenol
- 50) 3-Ethyl-5-methyl-4-(4-(4-(1-piperidinylcarbonyl)phenoxy)butyloxy)-phenol

The following is a production example for the compounds of the general
10 formula [VIII], which are intermediates for the production of the compounds of the present invention.

Intermediate Production Example 5

A reaction vessel was charged with 30.5 g of 4-hydroxyphenyl benzoate, 21.6 g of potassium carbonate, 20.8 g of 1,1,3-trichloropropene and 100 ml of N,N-di-
15 methylformamide. After stirring at room temperature for 15 hours, the reaction mixture was poured into water and extracted twice with 150 ml of diethyl ether. The ether layers were combined, washed with water, dried over anhydrous magnesium sulfate and then concentrated to give a crude product. The crude product was subjected to silica gel chromatography, which afforded 44.1 g of 4-(3,3-dichloro-2-propenyloxy)phenyl benzoate
20 (yield, 96%).

A reaction vessel was charged with 44.1 g of 4-(3,3-dichloro-2-propenyl-oxy)phenyl benzoate and 400 ml of methanol, to which 33 g of 30% potassium hydroxide solution was slowly added dropwise under ice cooling. After stirring for 1 hour, the reaction mixture was weakly acidified by the addition of 10% hydrochloric acid and
25 extracted twice with 150 ml of diethyl ether under salting out. The ether layers were combined, washed with water, dried over anhydrous magnesium sulfate and then concentrated to give a crude product. The crude product was subjected to silica gel chromatography, which afforded 26.0 g of 4-(3,3-dichloro-2-propenyloxy)phenol (yield, 87%).

A reaction vessel was charged with 26.0 g of 4-(3,3-dichloro-2-propenyloxy)-phenol and 500 ml of carbon tetrachloride, to which a solution of 27.1 g of tert-butyl hypochlorite dissolved in 20 ml of carbon tetrachloride was slowly added dropwise. After 24 hours, the reaction mixture was poured into water and the organic layer (carbon
5 tetrachloride layer) was separated. The organic layer was washed with water, dried over anhydrous magnesium sulfate and then concentrated to give a crude product. The crude product was subjected to silica gel chromatography, which afforded 11.0 g of 2,6-dichloro-4-(3,3-dichloro-2-propenyloxy)phenol (yield, 32%), $n_D^{22.5}$ 1.5895.

The following are production examples for the compounds of the general
10 formula [XI], which are intermediates for the production of the compounds of the present invention.

Intermediate Production Example 6

A reaction vessel was charged with 10.6 g of 1,3-dibromopropane, 5.53 g of potassium carbonate and 100 ml of N,N-dimethylformamide, to which a solution of
15 30.5 g of 2,6-dichloro-4-(3,3-dichloro-2-propenyloxy)phenol dissolved in 40 ml of N,N-dimethylformamide was slowly added dropwise. After stirring at room temperature for 24 hours, the reaction mixture was poured into water and extracted twice with 150 ml of diethyl ether. The ether layers were combined, washed with water, dried over anhydrous magnesium sulfate and then concentrated to give a crude product. The crude product was
20 subjected to silica gel chromatography, which afforded 11.1 g of 3,5-dichloro-4-(3-bromopropoxy)-1-(3,3-dichloro-2-propenyloxy)benzene (yield, 77%), $n_D^{24.0}$ 1.5693.

Intermediate Production Example 7

A reaction vessel was charged with 22.67 g of 1,4-dibromobutane, 11.06 g of potassium carbonate and 200 ml of N,N-dimethylformamide, to which a solution of
25 20.16 g of 2,6-dichloro-4-(3,3-dichloro-2-propenyloxy)phenol dissolved in 80 ml of N,N-dimethylformamide was slowly added dropwise. After stirring at room temperature for 24 hours, the reaction mixture was poured into water and extracted twice with 300 ml of diethyl ether. The ether layers were combined, washed with water, dried over

anhydrous magnesium sulfate and then concentrated to give a crude product. The crude product was subjected to silica gel chromatography, which afforded 21.77 g of 3,5-dichloro-4-(4-bromobutyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene (yield, 74%), $n_D^{25.0}$ 1.5666.

- 5 The following is a production example for the compounds of the general formula [XII], which are intermediates for the production of the compounds of the present invention.

Intermediate Production Example 8

- A reaction vessel was charged with 22.8 g of methyl 4-hydroxybenzoate,
10 23.5 g of potassium carbonate, 25.7 g of benzyl bromide and 250 ml of N,N-dimethylformamide. After stirring at room temperature for 24 hours, the reaction mixture was filtered through celite. The filtrate was poured into water and extracted twice with diethyl ether. The ether layers were combined, washed with water, dried over anhydrous magnesium sulfate and then concentrated, which afforded 35.5 g of methyl 4-benzyloxybenzoate (yield, 97%).
15

- A reaction vessel was charged with 34.7 g of methyl 4-benzyloxybenzoate and 200 ml of methanol, to which 85 ml of 20% aqueous potassium hydroxide solution was added at room temperature. After stirring for 1 hour, the reaction mixture was weakly acidified by the addition of 10% hydrochloric acid, and the precipitated crystals
20 were collected by filtration. The crystals thus obtained were washed with 10% hydrochloric acid and then water, and dried, which afforded 33.3 g of 4-benzyloxybenzoic acid (yield, 102%).

- A reaction vessel was charged with 5.71 g of 4-benzyloxybenzoic acid and 60 ml of hexane, to which 7.01 g of thionyl chloride was added dropwise with stirring at
25 room temperature. After stirring for 2 hours with heating under reflux, the reaction mixture was slowly cooled, and the precipitated crystals were collected by filtration. The crystals thus obtained were washed with hexane and dried, which afforded 5.34 g of 4-benzyloxybenzoyl chloride (yield, 86%).

A reaction vessel was charged with 2.23 g of dipropylamine and 20 ml of dichloromethane, to which a mixture of 2.47 g of 4-benzyloxybenzoyl chloride and 10 ml of dichloromethane was slowly added dropwise under ice cooling. After stirring at room temperature for 2 hours, the solvent was distilled out, and 10% hydrochloric acid was
5 poured into the residue. The mixture was extracted twice with ethyl acetate. The ethyl acetate layers were combined, washed with saturated aqueous sodium hydrogencarbonate solution and then water, dried over anhydrous magnesium sulfate and then concentrated, which afforded 2.69 g of 4-(N,N-dipropylcarbamoyl)-1-benzyloxybenzene (yield, 86%).

A reaction vessel was charged with 2.49 g of 4-(N,N-dipropylcarbamoyl)-1-
10 benzyloxybenzene and 30 ml of ethyl acetate. The air in the reaction vessel was replaced with nitrogen gas. To the vessel was added 0.2 g of 10% palladium on carbon, and the nitrogen gas in the vessel was replaced with hydrogen gas, followed by vigorous stirring at room temperature for 2 hours. The hydrogen gas in the vessel was replaced with nitrogen gas, and the reaction mixture was filtered through celite. The residual solid
15 materials were washed with methanol and the filtrate was concentrated, which afforded 1.68 g of 4-(N,N-dipropylcarbamoyl)phenol (yield, 95%), m.p., 92.7°C.

The following is a production example for the compounds of the general formula [IX], which are intermediates for the production of the compounds of the present invention.

20 Intermediate Production Example 9

A reaction vessel is charged with 8.08 g of 1,3-dibromopropane, 3.04 g of potassium carbonate and 100 ml of N,N-dimethylformamide, to which a solution of 4.43 g of 4-(N,N-dipropylcarbamoyl)phenol dissolved in 50 ml of N,N-dimethylform-
25 amide is added dropwise at room temperature for 2 hours. After stirring at room temperature for 24 hours, the reaction mixture is filtered through celite. The filtrate is poured into water and extracted twice with ethyl acetate. The ethyl acetate layers are combined, washed with water, dried over anhydrous magnesium sulfate and then concentrated to give a crude product. The crude product is subjected to silica gel chromatography, which

afforded 4-(N,N-dipropylcarbamoyl)-1-(3-bromopropoxy)benzene.

The following are formulation examples in which "parts" are by weight and the present compounds are designated by their compound numbers as described above.

Formulation Example 1: Emulsifiable concentrates

- 5 Ten parts of each of the present compounds (1) to (38) are dissolved in 35 parts of xylene and 35 parts of N,N-dimethylformamide, to which 14 parts of polyoxy-ethylene styrylphenyl ether and 6 parts of calcium dodecylbenzenesulfonate are added, and the mixture is well stirred to give a 10% emulsifiable concentrate of each compound.

Formulation Example 2: Wettable powders

- 10 Twenty parts of each of the present compounds (1) to (38) are added to a mixture of 4 parts of sodium lauryl sulfate, 2 parts of calcium lignin sulfonate, 20 parts of synthetic hydrated silicon oxide fine powder and 54 parts of diatomaceous earth, and the mixture is stirred with a mixer to give a 20% wettable powder of each compound.

Formulation Example 3: Granules

- 15 To five parts of each of the present compounds (1) to (38) are added 5 parts of synthetic hydrated silicon oxide fine powder, 5 parts of sodium dodecylbenzene-sulfonate, 30 parts of bentonite and 55 parts of clay, and the mixture is well stirred. A suitable amount of water is then added to the mixture, which is further stirred, granulated with a granulator and then air-dried to give a 5% granule of each compound.

20 Formulation Example 4: Dusts

One part of each of the present compounds (1) to (38) is dissolved in a suitable amount of acetone, to which 5 parts of synthetic hydrated silicon oxide fine powder, 0.3 part of PAP and 93.7 parts of clay are added, and the mixture is stirred with a mixer. The removal of acetone by evaporation gives a 1% dust of each compound.

25 Formulation Example 5: Flowables

Twenty parts of each of the present compounds (1) to (38) are mixed with 1.5 parts of sorbitan trioleate and 28.5 parts of an aqueous solution containing 2 parts of polyvinyl alcohol, and the mixture is pulverized into fine particles having a particle size of

not more than 3 μm with a sand grinder, to which 40 parts of an aqueous solution containing 0.05 part of xanthan gum and 0.1 part of aluminum magnesium silicate is added and then 10 parts of propylene glycol is added. The mixture is stirred to give a 20% water-based suspension of each compound.

5 Formulation Example 6: Oil sprays

First, 0.1 part of each of the present compounds (1) to (38) is dissolved in 5 parts of xylene and 5 parts of trichloroethane. The solution was then mixed with 89.9 parts of deodorized kerosine to give a 0.1% oil spray of each compound.

 Formulation Example 7: Oil-based aerosols

10 First, 0.1 part of each of the present compounds (1) to (38), 0.2 part of tetramethrin, 0.1 part of d-phenothrin, and 10 parts of trichloroethane are dissolved in 59.6 parts of deodorized kerosine, and the solution is put in an aerosol vessel. The vessel is then equipped with a valve, through which 30 parts of a propellant (liquefied petroleum gas) is charged under increased pressure to give an oil-based aerosol of each compound.

15 Formulation Example 8: Water-based aerosols

 An aerosol vessel is filled with 50 parts of pure water and a mixture of 0.2 part of each of the present compounds (1) to (38), 0.2 part of d-allethrin, 0.2 part of d-phenothrin, 5 parts of xylene, 3.4 parts of deodorized kerosine and 1 part of an emulsifier [ATMOS 300 (registered trade name by Atlas Chemical Co.)]. The vessel is then
20 equipped with a valve, through which 40 parts of a propellant (liquefied petroleum gas) are charged under increased pressure to give a water-based aerosol of each compound.

 Formulation Example 9: Mosquito-coils

 First, 0.3 g of each of the present compounds (1) to (38) is mixed with 0.3 g of d-allethrin, and the mixture is dissolved in 20 ml of acetone. The solution is uniformly
25 mixed with 99.4 g of a carrier for mosquito-coils (prepared by mixing Tabu powder, pyrethrum marc powder and wood flour in the ratio of 4 : 3 : 3) under stirring. The mixture is well kneaded with 120 ml of water, molded and dried to give a mosquito-coil of each compound.

Formulation Example 10: Electric mosquito-mats

First, 0.4 g of each of the present compounds (1) to (38), 0.3 parts of d-allethrin and 0.4 g of pipenyl butoxide are dissolved in acetone to have a total volume of 10 ml. Then, 0.5 ml of the solution is uniformly absorbed in a substrate for electric mosquito-mats having a size of 2.5 cm x 1.5 cm x 0.3 cm (prepared by forming a fibrillated mixture of cotton linter and pulp into a sheet) to give an electric mosquito-mat of each compound.

Formulation Example 11: Heating smoke formulations

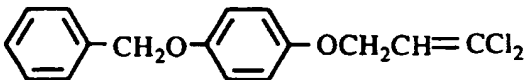
First, 100 mg of each of the present compounds (1) to (38) is dissolved in a suitable amount of acetone. The solution is absorbed in a porous ceramic plate having a size of 4.0 cm x 4.0 cm x 1.2 cm to give a heating smoke formulation of each compound.

Formulation Example 12: Poison baits

First, 10 mg of each of the present compounds (1) to (38) is dissolved in 0.5 ml of acetone, and the solution is uniformly mixed with 5 g of solid bait powder for animals (Breeding Solid Feed Powder CE-2, trade name by Japan Clea Co., Ltd.). The subsequent removal of acetone by air drying gives a 0.5% poison bait of each compound.

The following test examples demonstrate that the present compounds are useful as active ingredients of insecticidal/acaricidal agents. In these test examples, the present compounds are designated by their compound numbers as describe above and the compounds used for comparison are designated by their compound symbols as shown in Table 7.

TABLE 7

Compound	Chemical structure	Remarks
(A)		Compound disclosed in JP-A 49-1526/1974, page 22

Test Example 1: Insecticidal test against *Spodoptera litura*

A 200-fold water dilution (500 ppm) of an emulsifiable concentrate of the test compound, which had been obtained according to Formulation Example 1, was absorbed at a volume of 2 ml in 13 g of an artificial diet for *Spodoptera litura*, which had been
5 prepared in a polyethylene cup having a diameter of 11 cm. Ten fourth-instar larvae of *Spodoptera litura* were set free in the cup. After 6 days, the survival of the larvae was examined to determine the mortality. The test was conducted in duplicate.

As a result, it was found that the present compounds (2)-(12) exhibited the mortality of 80% or more. In contrast, compound (A) used for comparison exhibited the
10 mortality of 0%.

Test Example 2: Insecticidal test against *Plutella xylostella*

An emulsifiable concentrate of the test compound, which had been obtained according to Formulation Example 1, was diluted with water and spreading agent RINOU (available from Nihon Noyaku K.K.) so that the concentration of active ingredient
15 became 500 ppm and the spreading agent was 1000-fold diluted. The dilution was sprayed over potted cabbages at the five leaf stage at a volume of 25 ml per pot. After air drying, ten third-instar larvae of *Plutella xylostella* were set free on each pot. After 4 days, the mortality was determined.

As a result, it was found that the present compounds (2), (3), (9) and (11)
20 exhibited the mortality of 80% or more. In contrast, compound (A) used for comparison exhibited the mortality of 0%.

Test Example 3: Insecticidal test against *Musca domestica*

The test compound was diluted with acetone to a prescribed concentration. The dilution was applied to the backs of the thoraces of female adult houseflies (*Musca
25 domestica*) at a ratio of 10 µg compound/0.5 µl acetone with a micro-dropping apparatus. After 72 hours, the mortality was determined. The test was conducted in triplicate with 10 flies per group.

As a result, it was found that the present compounds (2), (3), (6), (7), (8),

(9), (10), (11) and (12) exhibited the mortality of 100%. In contrast, compound (A) used for comparison exhibited the mortality of 3.3%.

Test Example 4: Acaricidal test against *Tetranychus urticae* Koch

Several 130 ml plastic cups were filled with sandy loam and seeded with
5 kidney bean (*Phaseolus vulgaris*) at a ratio of two seeds per cup, which were cultivated in
a growth room until the primary leaves developed. The resulting seedlings of kidney
bean received adults of *Tetranychus urticae* Koch, which were kept and grown in a
greenhouse for 6 days. A water dilution (500 ppm) of an emulsifiable concentrate of the
test compound, which had been obtained according to Formulation Example 1, was
10 sufficiently sprayed over the leaves and stems of the seedlings. After keeping in the
greenhouse for 8 days, the survival of the adults was examined to determine the mortality.

As a result, it was found that the present compounds (1), (2), (3) and (6)
exhibited the mortality of 60% or more. In contrast, compound (A) used for comparison
exhibited the mortality of 0%.

15 Test Example 5: Insecticidal test against *Heliothis virescens*

An artificial diet was treated by incorporation of a water dilution (100 ppm) of
an emulsifiable concentrate of the test compound, which had been obtained according to
Formulation Example 1, at a volume of 0.2 ml. The treated diet was fed to second-instar
larvae of *Heliothis virescens*, which were then kept in a plastic box. After 6 or 7 days,
20 the mortality was determined. The test was conducted with 10 larvae per group.

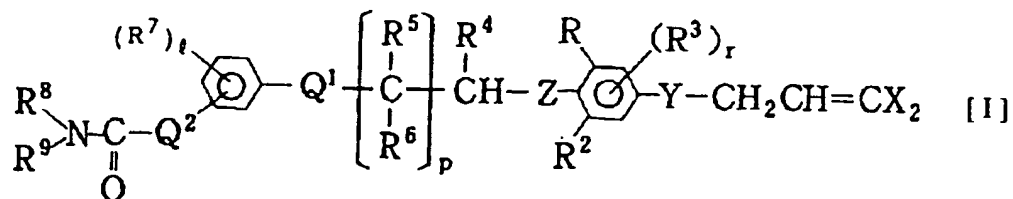
As a result, it was found that the present compounds (8) and (11) exhibited
the mortality of 80% or more. In contrast, compound (A) used for comparison exhibited
the mortality of 0%.

Industrial Applicability

25 The present compounds have excellent insecticidal/acaricidal activity, so that
they are satisfactorily effective for the control of noxious insects, mites and ticks.

CLAIMS

1. A dihalopropene compound of the general formula:



wherein R, R² and R³ are each independently halogen, C₁-C₃ haloalkyl or C₁-C₃ alkyl;

5 R⁴ is hydrogen or C₁-C₃ alkyl;

R⁵ and R⁶ are each independently hydrogen, C₁-C₃ alkyl or trifluoromethyl;

R⁷ is halogen, C₁-C₃ alkyl or trifluoromethyl;

R⁸ and R⁹ are each independently hydrogen, C₁-C₆ alkyl, C₁-C₃ haloalkyl, C₃-C₆ alkenyl, C₃-C₆ haloalkenyl, C₃-C₄ alkynyl, C₃-C₄ haloalkynyl, C₄-C₈ cycloalkyl-
10 alkyl, C₆-C₈ cycloalkenylalkyl or C₃-C₄ alkoxyalkyl;

or C₃-C₆ cycloalkynyl optionally substituted with C₁-C₂ alkyl,

or R⁸ and R⁹ are combined together at their ends to form C₂-C₆ alkylene optionally substituted with C₁-C₂ alkyl, or C₄-C₆ alkenylene optionally substituted with C₁-C₂ alkyl;

15 Q¹ is a single bond or T;

T is a group of the general formula:



wherein R¹⁰ and R¹¹ are each independently hydrogen, C₁-C₃ alkyl or trifluoromethyl; A is oxygen, S(O)_n, NR¹², C(=O)G or GC(=O) in which n is an integer of 0 to 2, R¹² is
20 hydrogen or C₁-C₃ alkyl, G is oxygen or NR¹³, and R¹³ is hydrogen or C₁-C₃ alkyl; and s is an integer of 0 to 6;

Q^2 is a single bond, oxygen or NR^{14} in which R^{14} is hydrogen or C_1-C_3 alkyl;

X's are each independently chlorine or bromine;

Y is oxygen, NH or sulfur;

5 Z is oxygen, sulfur or NR^{15} in which R^{15} is hydrogen or C_1-C_3 alkyl;

l is an integer of 0 to 4;

p is an integer of 0 to 6; and

r is an integer of 0 to 2.

2. A dihalopropene compound according to claim 1, wherein R and R^2 are
10 each independently halogen or C_1-C_3 alkyl, and r is 0.

3. A dihalopropene compound according to claim 1, wherein R and R^2 are each independently halogen or C_1-C_3 alkyl, and r is 1 or 2.

4. A dihalopropene compound according to claim 1, wherein R and R^2 are each independently chlorine, bromine or C_1-C_3 alkyl, and r is 0.

15 5. A dihalopropene compound according to claim 1, wherein R and R^2 are both chlorine and r is 0.

6. A dihalopropene compound according to claim 1, wherein Y and Z are both oxygen.

7. A dihalopropene compound according to claim 4, wherein Y and Z are
20 both oxygen.

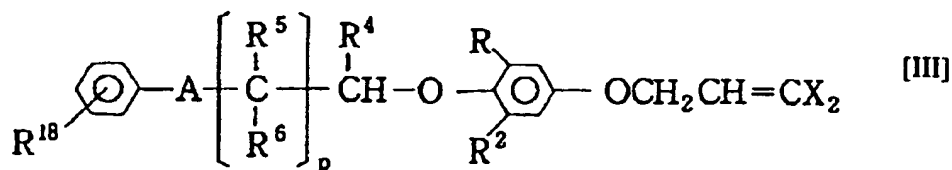
8. A dihalopropene compound according to claim 5, wherein Y and Z are both oxygen.

9. A dihalopropene compound according claim 1, wherein Q^1 is a single bond.

25 10. A dihalopropene compound according to claim 1, wherein Q^1 is T and s is 0.

11. A dihalopropene compound according to claim 1, wherein Q^1 is T and s is an integer of 1 to 6.

12. A dihalopropene compound according claim 1, wherein Q^2 is a single bond.
13. A dihalopropene compound according to claim 1, wherein Q^2 is oxygen.
- 5 14. A dihalopropene compound according to claim 1, wherein Q^2 is NR^{14} .
15. A dihalopropene compound according to claim 7, wherein Q^1 is T, s is 0, and Q^2 is a single bond.
16. A dihalopropene compound according to claim 15, wherein A is oxygen.
- 10 17. A dihalopropene compound according to claim 8, wherein Q^1 is T, s is 0, and Q^2 is a single bond.
18. A dihalopropene compound according to claim 17, wherein A is oxygen, l is 0, p is an integer of 2 to 4, and R^4 , R^5 and R^6 are all hydrogen.
19. A dihalopropene compound according to claim 18, wherein R^8 and R^9
- 15 are each independently hydrogen, C_1 - C_6 alkyl, C_3 - C_6 alkenyl or C_3 - C_4 alkynyl, or R^8 and R^9 are combined together at their ends to form ethylene, trimethylene, tetramethylene, pentamethylene or butenylene.
20. An insecticidal/acaricidal agent comprising, as an active ingredient, a dihalopropene compound according to any of claims 1 to 19.
- 20 21. A compound of the general formula:



wherein R and R^2 are each independently halogen, C_1 - C_3 haloalkyl or C_1 - C_3 alkyl;

R^4 is hydrogen or C_1 - C_3 alkyl;

R^5 and R^6 are each independently hydrogen, C_1 - C_3 alkyl or trifluoromethyl;

25 R^{18} is carboxyl or amino;

A is oxygen, $S(O)_n$, NR^{12} , $C(=O)G$ or $GC(=O)$ in which n is an integer of 0 to 2, R^{12} is hydrogen or C_1 - C_3 alkyl, G is oxygen or NR^{13} , and R^{13} is hydrogen or C_1 - C_3 alkyl;

X's are each independently chlorine or bromine; and

5 p is an integer of 0 to 6.

22. A compound according to claim 21, wherein R^{18} is carboxyl.

23. A compound according to claim 22, wherein A is oxygen.

24. A compound according to claim 23, wherein R and R^2 are each independently halogen or C_1 - C_3 alkyl, R^4 , R^5 and R^6 are all hydrogen, and p is 2 or 3.

10 25. 4-(3-(2,6-Dichloro-4-(3,3-dichloro-2-propenyloxy)phenoxy)propyloxy)benzoic acid.

26. 3-(3-(2,6-Dichloro-4-(3,3-dichloro-2-propenyloxy)phenoxy)propyloxy)benzoic acid.

15 27. 2-(3-(2,6-Dichloro-4-(3,3-dichloro-2-propenyloxy)phenoxy)propyloxy)benzoic acid.

28. 3,5-Dichloro-4-(4-(4-aminophenoxy)butyloxy)-1-(3,3-dichloro-2-propenyloxy)benzene.